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## **POTENTIALLY HAZARDOUS MATERIALS**

National Aeronautics and Space Administration

Responsible Office: Safety and Mission Assurance Office

#### **PREFACE**

This Langley Research Center (LaRC) Procedural Requirements (LPR) identifies responsibilities, and procedures for the safe use of PHM's. It implements the Occupational Safety and Health (OSHA) Hazard Communication Standard and the Chemical Laboratory Standard.

The procedural requirements contained herein do not in any way relieve supervisors and employees from their responsibility for the conduct of safe operations.

LAPG 1710.12 dated July 1999, is rescinded and should be destroyed.

Delma C. Freeman, Jr. Deputy Director

#### DISTRIBUTION

SDL 040, SDL 043, SDL 410, SDL 411, and SDL 412 (LaRC Safety Manual Holders) 429/Safety and Facility Assurance Branch (SFAB, 200 copies)

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#### **AUTHORITY**

ANSI 2400.1 - 1993 Guidelines.

ANSI Z400.1, Standard for the Preparation of Material Safety Data Sheets.

ANSI Standard Z87. 1, Protective Eyewear.

Department of Defense (DOD) - Military air specifications, Air Force Manual (AFM) 71-4, "Packaging and Handling of Dangerous Materials for Transportation by Military Aircraft" (ref. 9).

Department of Transportation (DOT) 49 CFR, Chapter 1, Research and Special Programs Administration, Department of Transportation.

DOT 49 CFR, Subchapter B, Hazardous Materials Regulations, Parts 171-177.

DOT 46 CFR, Shipping.

DOT Specification 4L, Land transportation.

Federal Aviation Administration (FAA) - Commercial air specifications, "Official Air Transport of Restricted Articles Tariff-6D" (ref. 8).

Federal Supply Class (FSC), FED-STD-313C, "Material Safety Data Sheets."

International Agency for Research on Cancer (IARC)

"Matheson Gas Data Book," "Handbook of Compressed Gas," "Encyclopedia of Chemical Technology."

National Fire Protection Association (NFPA), <u>Fire Protection Guide on Hazardous Materials</u>, Emergency Response Guidebook, DOT P5800.5 and NFPA 325M.

NFPA Handbook 704, "Standard System for the Identification of Hazardous Materials for Emergency Response,"

NFPA 50A and NFPA 50B

NFPA 77, Standard on Static Electricity.

National Toxicology Program (NTP).

Occupational Safety and Health Administration (OSHA) 29 Code of Federal Regulation (CFR) 1910.1450, Chemical Laboratory Standard.

OSHA 29 CFR 1910.1200, Hazardous Communication Standard.

OSHA 29 CFR 1910.1450 Appendix B, References, (Non-Mandatory).

OSHA 29 CFR 1910.1450, Occupational Exposure to Hazardous Chemicals in Laboratories.

OSHA/National Institute of Occupational Safety and Health Pocket Guide to Chemical Hazards: "Purple Book," June 1990, and "Orange Book", June 1994.

United States Coast Guard (USCG) - Waterways specifications-Refer to DOT Regulations and Coast Guard Regulation CF-108 (ref. 10), for packaging and handling information.

#### **REFERENCES**

LAPD 1150.2, "Boards, Panels, Committees, Councils, and Teams."

LAPD 1700.1, "Safety Program."

LAPD 1700.2, "Safety Assignments."

LPR 1710.4, "Personnel Protection - Clothing and Equipment."

LPR 1710.5, "Ionizing Radiation."

LPR 1710.7, "Use and Handling of Explosives and Pyrotechnics."

LPR 1710.40, "Safety Regulations Covering Pressurized Systems."

LPR 1740.5, "Procedures for Cleaning of Systems and Equipment for Oxygen Service."

LPR 1740.6, "Personnel Safety Certification."

LPR 8800.1, "Environmental Program Manual".

Langley Management System (LMS) CP-4505, "Prepare Purchase Request (PR) and Supporting Documents."

LMS-CP-2701, "LaRC Directives Initiation, Review and Approval."

LMS-CP-4540, "Procurement Purchase Card."

LMS-CP-4703, " Review of Purchase Requests by the Safety and Mission Assurance Office (SMAO)."

LMS-CP-4759, "Receipt, Handling, Storage, Marking, Preservation and Delivery of Hazardous Materials."

LMS-CP-4760, "Reporting Injuries, Illnesses, Compensation Claims and Unsafe Working Conditions."

NASA Langley Form 44, "Hazardous Material--Procurement, Inventory, and Storage Record."

NASA Langley Form 44B, "Hazardous Materials - Reissue Record."

NASA Langley Form 52, "Shipping/Transfer Document."

NASA Langley Form 52B, "Shipping Document for Noncontrolled Property (Not to be used for shipping under P.O., Contract, Grant, MOE or Loan,"

NASA Langley Form 62, "Chemical Worker's Certification Card."

NASA Langley Form 66, "Worker Appointment and Certification Form."

NASA Langley Form 118, "Safety Permit Request - Hazardous Materials."

NASA Langley Form 125, "Purchase Request/Purchase Order (PR/PO)."

NASA Langley Form 131, "Receipt and Inspection Report (Nonstocked Items)."

NASA Langley Form 175, "Material Safety Data Sheet Review Request."

NASA Langley Form 498, "Safety Permit."

Chapter 1

#### 1. INTRODUCTION

Potentially Hazardous Material (PHM) is defined as any substance having intrinsic properties which can pose a risk of injury or illness to personnel or of destruction of property. That is, any material which is a health or physical hazard. Specifically, provisions of these procedural requirements are applicable to materials having toxic, flammable, corrosive, cryogenic, or asphyxiation properties. Radioactive and pyrotechnic materials are not included as they are covered in LPR 1710.5, "Ionizing Radiation," and LPR 1710.7, "Use and Handling of Explosives and Pyrotechnics," respectively.

PHM includes those substances defined by Occupational Health and Safety Administration (OSHA) as hazardous chemicals. The OSHA definition includes as hazardous chemicals those for which there is statistically significant evidence, based on at least one study conducted in accordance with established scientific principles, that acute or chronic health effects may occur in exposed employees. OSHA includes in its definition hazardous chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes. (See 29 CFR 1910.1450, Part b.)

#### 1.1 PURPOSE

The purpose of these procedural requirements is to define organization and procedures for the safe use of PHM and to facilitate compliance with regulations promulgated by the OSHA and other consensus standards as may be appropriate at LaRC.

These procedural requirements implement OSHA's Hazard Communication Standard (29 Code of Federal Regulations [CFR] 1910.1200) and Chemical Laboratory Standard (29 CFR 1910.1450). These procedural requirements outline the procedures to be followed to obtain and maintain information on hazardous materials and in training workers on the use of this information.

These procedural requirements describe organization, responsibilities, and administrative procedures for acquisition and use of hazardous materials. A permit system shall be used for highly hazardous materials including carcinogens and highly toxic gases.

General and specific health and safety information for various classes of PHM's are included in these procedural requirements. This LPR is to be used as a general reference and is not intended to necessarily furnish all information required to plan and execute safe operation for a given material. A list of sources of additional information is provided and maintained by the Safety and Facility Assurance Branch (SFAB), Safety and Mission Assurance Office (SMAO).

These procedural requirements do not intend to address all procedures and laws for hazardous materials. For example, there are Department of Transportation shipping regulations for chemicals sent off LaRC. For technical assistance in this area, contact the Transportation Officer, Logistics Management Team (LMT). Environmental laws and requirements concerning the manufacture, emission, and disposal of hazardous materials are not detailed in these procedural requirements, but are presented in LPR 8800.1, "Environmental Program Manual." For technical assistance on environmental requirements contact the Environmental Management Team (EMT).

#### 1.2 APPLICABILITY AND AUTHORITY

The provisions of these procedural requirements are applicable within the LaRC organizational elements to both NASA contractors and resident organizations directly concerned with the procurement, handling, use, storage, disposal, and inspection of PHM's. Training of workers to meet basic hazard communication and laboratory standard requirements shall be done by NASA for civil servant employees and by contractors for their employees. As a minimum, contractor requirements shall be in accordance with the LaRC requirements as described in these procedural requirements.

#### 1.3 ISSUANCE AND CONTROL

Revisions to these procedural requirements shall be developed by the LaRC Potentially Hazardous Materials Committee (PHMC) in accordance with LAPD 1150.2, "Boards, Panels, Committees, Councils, and Teams." Specific changes shall be reviewed, approved and distributed in accordance with LMS-CP-2701, "LaRC Directives Initiation, Review and Approval."

#### 1.4 DEFINITIONS AND TERMINOLOGY

Appendix B contains definitions and terminology used in these procedural requirements.

#### 1.5 RECORDS

The following forms were completed when implementing requirements:

NASA Langley Form 44, "Hazardous Material--Procurement, Inventory, and Storage Record."

NASA Langley Form 44B, "Hazardous Materials - Reissue Record."

NASA Langley Form 52, "Shipping/Transfer Document."

NASA Langley Form 52B, "Shipping Document for Noncontrolled Property (Not to be used for shipping under P.O., Contract, Grant, MOE or Loan,"

NASA Langley Form 62, "Chemical Worker's Certification Card."

NASA Langley Form 66, "Worker Appointment and Certification Form."

NASA Langley Form 118, "Safety Permit Request - Hazardous Materials."

NASA Langley Form 125, "Purchase Request/Purchase Order (PR/PO)."

NASA Langley Form 131, "Receipt and Inspection Report (Nonstocked Items)."

NASA Langley Form 175, "Material Safety Data Sheet Review Request."

NASA Langley Form 498, "Safety Permit."

Chapter 2

#### 2. RESPONSIBILITIES

## 2.1 POTENTIALLY HAZARDOUS MATERIALS COMMITTEE (PHMC)

The PHMC is established under the authority of LAPD 1700.1, "Safety Program," and LAPD 1150.2, "Boards, Panels, Committees, Councils, and Teams." Any member of this committee is authorized to investigate any questionable use of a PHM, act in the name of the Center Director to stop work or to prevent use of the material, which is considered unsafe, and initiate action to eliminate the unsafe condition. Such action shall be documented within 24 hours by formal letter to the Chairperson, PHMC. However, if line management is not in agreement with the corrective action recommended by the official who stopped the work, these reasons shall be submitted to the Chairperson, Executive Safety Board (ESB), who shall make an appropriate review. In these cases, work shall not resume without the approval of the Chairperson, ESB.

Due to the need for the PHMC to maintain an overview of operations at LaRC involving PHM's, a review system has been established. This review system includes NASA Langley Form 498, "Safety Permit" which is described in Chapter 5. NASA Langley Form 498's are required before operations commence.

The PHMC shall also overview the activities of the Pyrotechnic Support Engineer for control of pyrotechnic materials.

## 2.1.1 Structure and Organization

The PHMC functions as a committee of the ESB. Its position in the organization for control of PHM's is shown in Figure 2.1. Committee members, including the Chairperson, shall be appointed by the ESB, by virtue of their technical and/or educational expertise in such areas as chemistry, hazardous gases, and compatibility of materials. Members are appointed to serve for a three-year term. During the first meeting of a new calendar year, the committee shall elect a committee secretary from its full membership. The committee secretary's responsibilities include preparing and distributing committee minutes in addition to all other functional responsibilities. Representatives of SFAB, SMAO shall serve as members of the committee. Typically, this representation shall consist of the LaRC Industrial Hygiene (IH) Contractor and the LaRC Safety Manager or the LaRC Safety Manager's representative.

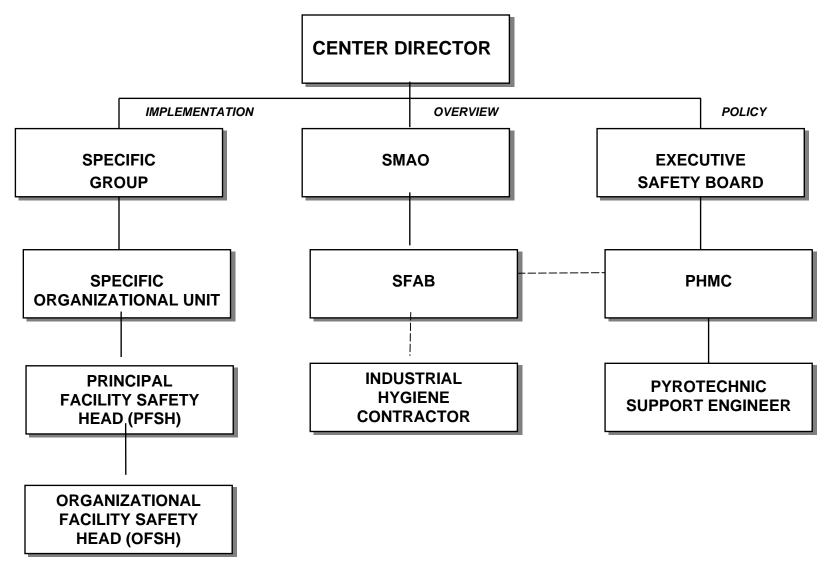


Figure 2.1, LaRC Organization for Control of Potentially Hazardous Materials.

## 2.1.2 Duties and Responsibilities

The duties and responsibilities of the committee are set forth in LAPD 1150.2. The committee functions as a review and guidance body providing recommendations in applicable areas as required. The committee shall:

- prepare and distribute minutes of committee meetings which shall contain, as a
  minimum, a record of persons present and a description of matters discussed
  and conclusions reached including the opinions of dissenting members, and
  copies of all reports issued or approved by the committee. Committee minutes
  shall be distributed to all members, the affected operations personnel, the
  Chairperson, ESB, and the Director, SMAO.
- carry on official correspondence for the committee as needed.

#### Membership duties are:

- Be cognizant of matters pertaining to use of PHM's at LaRC. This is chiefly, but not entirely, achieved by attending the committee meetings and participating in the decisions made by the committee.
- Serve on ad hoc committees, which are appointed by the Chairperson as needed.

#### 2.2 SAFETY AND HEALTH FUNCTIONS

The primary responsibility for safe use of PHM's lies with the individual user. Although this responsibility cannot be delegated, various LaRC functions provide planning, management, and assistance.

## 2.2.1 Facility Safety Head (FSH)/Chemical Hygiene Officer (CHO)

The prime responsibilities of the FSH are the safe operation of the research apparatus and maintenance of a safe working environment. The scope of this responsibility encompasses such elements as the establishment and use of normal and emergency operating procedures, configuration control, safety training, preventative maintenance, and the other traditional institutional types of safety considerations.

The FSH may appoint an Organizational Facility Safety Head (OFSH) for each operation that is functionally or generically distinct. Procedures for appointments are presented in LAPD 1700.2, "Safety Assignments." The FSH or OFSH shall, in each case, be a representative of line management who is thoroughly familiar with the operation.

FSH's and/or OFSH's shall be familiar with any NASA Langley Form 498's issued for their facilities. For laboratories operating under a Chemical Hygiene Plan (CHP), the FSH is the CHO. The CHO is an employee who is qualified by training or experience to provide technical guidance in the development and implementation of the provisions of the Chemical Hygiene Plan and applicable NASA Langley Form 498's.

#### 2.2.1.1 Interfaces

The FSH or OFSH of the facility where the PHM is to be used shall be the first point of contact for the individual who has need for procurement, use, storage, or disposal of PHM. The first point of contact for the FSH or OFSH for assistance with use of PHM's shall be the LaRC IH Contractor.

## 2.2.1.2 Responsibilities

The basic responsibilities of the FSH or OFSH are described in LAPD 1700.2. The FSH or OFSH shall implement these responsibilities for safe use of PHM's:

- Establish and review normal and emergency operating procedures. These
  procedures shall include cleanup of Class I ("Hazardous Material Spill Control
  and Contingency Plan") spills by facility personnel (normally, the using agency).
  Class II ("Hazardous Material Spill Control and Contingency Plan") spill
  assistance shall be sought from the LaRC Safety Manager (Chapter 2.2.4). All
  spills shall be reported to the LaRC Safety Manager.
- Supervise and coordinate the procurement, use, storage, and disposal of PHM's. Guidelines for the initial identification and procurement of hazardous materials are contained here in Chapter 2. Disposal is covered in detail in LPR 8800.1 and is mentioned here in Chapter 6.
- Maintain an inventory of such materials. This shall be one central file for the facility. The inventory of materials required to meet these procedural requirements and OSHA requirements may be the same list used for environmental requirements (e. g., chemical identification, quantity on hand).
- Maintain a file of Material Safety Data Sheets (MSDS's), (Chapter 4) of all PHM's used in the facility. This MSDS file shall be one central file, (several small files in separate work areas in a large facility is permitted). The FSH shall determine the appropriate file location(s). Guidelines for these files are as follows:
  - These files shall include all appropriate MSDS's. For example, several vendor containers of 100 percent Acetone need only one MSDS since its chemical makeup does not vary. However, files for the generic class "cleaning solvent" or class "black enamel paint, spray, 16 ounce," may contain several MSDS's for each of these items because several vendors may have supplied similar materials. The MSDS may vary from vendor to vendor since the chemicals, and hazards, will differ. AN MSDS IS REQUIRED FOR EACH POTENTIALLY HAZARDOUS CHEMICAL PRESENT. This MSDS requirement includes "free" vendor samples as well as LaRC research and development test chemicals in use outside of their manufacturing location (e.g., lab hood, batch processor).
  - The MSDS file(s) shall be accessible to all employees working in the facility and its location(s) shall be made known.
  - Exceptions exist for maintenance of MSDS files under the chemical laboratory standard. Laboratories operating under a NASA Langley Form 498 shall maintain documentation on basic hazardous materials produced. The

- chemical lab safety program relies on process control through procedures, rather than identification of all hazardous components.
- Hazardous materials including research and development (R&D) chemicals produced for processing or evaluation in facilities other than the point of manufacture shall have an MSDS completed, with one copy being forwarded for hazard review to the LaRC IH Contractor for PHMC and SFAB, SMAO review (Chapter 4).
- Ensure that all employees who routinely work in the facility are aware of the physical or chemical hazards of the materials they routinely work with, and other hazardous materials in the facility that they may encounter in any foreseeable emergency. For facilities with highly toxic substances in use or in storage, visitors shall be apprised of special facility emergency procedures in the event of leaks or spills. For example, if warning lights are used to indicate hazardous conditions, visitors (including other on-site LaRC personnel who may periodically enter the facility) shall be informed of the meaning of the warning light and appropriate actions. Warning lights, bells, and so forth, shall include signs indicating the purpose of the alarm (i.e., "Fluorine Gas Alarm").
- Provide or acquire periodic refresher training to workers whenever significant changes occur for chemicals in use in the facility.
- Maintain a current list of employees in the organization who are trained and certified to use materials under NASA Langley Form 498 (Chapter 5).
- Ensure capabilities and procedures exist in the facility for cleanup of Class I spills
  of hazardous materials. Seek the assistance of the EMT and the LaRC Safety
  Manager's staff for containment and cleanup assistance of Class III spills
  involving hazardous materials. A list of Class H chemicals is contained in
  Appendix B of LPR 8800.1, "Environmental Program Manual."
- Accompany SFAB, SMAO, personnel and representatives during all surveys and audits of the organization.

## 2.2.2 Facility Coordinator (FC)

In the absence of the FSH, the Facility Coordinator (FC) shall accompany SFAB, SMAO, personnel during surveys and audits of the organization.

## 2.2.3 LaRC Industrial Hygiene (IH) Contractor

The LaRC IH Contractor has specific interfaces and responsibilities with regard to PHM.

#### 2.2.3.1 Interfaces

The LaRC IH Contractor reports directly to the LaRC Safety Manager and serves on the PHMC. The LaRC IH Contractor shall be the primary committee contact for on-site users of potentially hazardous material.

## 2.2.3.2 Responsibilities

The LaRC IH Contractor's responsibilities are to:

 provide technical and administrative guidance to LaRC personnel for the safe use of potentially hazardous material where such material may pose a health hazard. Assist personnel in the interpretation of MSDS technical data.

- provide monitoring services to document personnel exposures. Results of these surveys shall be provided to the individual (or to the facility for posting) within 15 days of receipt of results from a laboratory doing the analysis.
- perform pre-operational surveys to identify potential health hazards and recommend control procedures. This shall include assisting in determination of industrial ventilation to control health hazards.
- perform periodic inspections to assure the effectiveness of control procedures and identify the need for a NASA Langley Form 498. Ventilation systems (fume hoods and paint booths) used to control health hazards shall be surveyed annually. Audit all NASA Langley Form 498's at least annually for compliance and periodically report results to the PHMC.
- provide training and indoctrination of personnel in health hazard control measures such as personal protective equipment (e.g., respirators, gloves).
- review potentially hazardous material purchase requests for compatibility with approved policies and procedures and to help identify changes in use, which may require new or additional health hazard control measures (Chapter 2).
- whenever possible, advise the LaRC Safety Manager of non-health related hazards associated with the use of potentially hazardous materials.
- advise the PHMC, the Occupational Health Services (OHS), and SFAB, SMAO of developments in statutory requirements and standards of good practice for control of potentially hazardous materials where such materials may pose health hazards.
- supply MSDS's, if available, from MSDS databases or assist in the acquisition and technical interpretation of proprietary or trade secret MSDS information.

## 2.2.4 LaRC Safety Manager (Head, SFAB, SMAO)

The LaRC Safety Manager has specific interfaces and responsibilities with regard to PHM.

#### 2.2.4.1 Interfaces

The LaRC Safety Manager shall:

- report directly to the Director, SMAO
- serve on the PHMC as a member (or assign a designee)
- be the principal LaRC contact with federal safety and health regulatory agencies.

## 2.2.4.2 Responsibilities

The responsibilities of the LaRC Safety Manager are described in LAPD 1700.2, Safety Assignments." The LaRC Safety Manager's responsibilities for safe use of PHM are to:

 provide technical and administrative guidance for the safe storage and use of PHM where such material poses hazards not primarily health related.

- evaluate the LaRC IH Contractor pre-operational audits to identify such hazards and control procedures.
- use annual facility Safety and Health audits to assure the effectiveness of NASA Langley Form 498 control measures.
- review training data and/or provide training and indoctrination of personnel through the LaRC IH Contractor, as needed, to assure understanding of the LaRC hazard communication policies.
- serve as final reviewing and/or certifying authority for the following:
  - NASA Langley Form 66, "Worker Appointment and Certification Form" (Chapter 5).
  - NASA Langley Form 44, "Hazardous Material--Procurement, Inventory, and Storage Record" (Chapter 3).
  - NASA Langley Form 498, "Safety Permit".
- provide assistance to facility personnel in Class H spills control (Class H spills are environmentally reportable) through the use of supplies and manpower available on-site or through prior planning and arrangements by SFAB, SMAO with off-site response teams. These activities are outlined in "Hazardous Material Spill Control and Contingency Plan," and LPR 8800.1, "Environmental Program Manual."

## 2.2.5 Safety Manager Designated Representative, SFAB, SMAO

In the absence of the LaRC Safety Manager in matters regarding PHM's, full signature authority shall be granted to the LaRC Safety Manager's appointed representative.

## 2.2.6 Occupational Health Services (OHS)

The OHS shall be the primary contact for LaRC employees for matters relating to occupational health. Responsibilities are described in LAPD 1700.2. The Director, OHS shall implement these responsibilities for the safe use of PHM's:

- recommend and implement medical surveillance of users of PHM's.
- maintain appropriate records of such surveillance.
- serve as a qualifying official on NASA Langley Form 66.
- notify the LaRC Safety Manager, SFAB, SMAO as soon as possible.
- stay alert for adverse health incidents, such as possible chemical related contact dermatitis, involving PHM's.

## 2.2.7 Logistics Management Team (LMT)

The Head of the LMT shall:

 maintain a file of MSDS's for all materials available through the stores stock, and provide a copy of the MSDS to users upon chemical issue.

- transmit to users a copy of the MSDS provided by suppliers for materials obtained by Purchase Request.
- attach NFPA 704A labels to items issued out of supply.

## 2.2.8 Individual Responsibilities

#### Individuals shall:

- participate in training. The Office of Human Resources (OHR) shall incorporate basic hazard communication training information into its NASA employee indoctrination program.
- review MSDS's prior to use of hazardous material. New MSDS's on existing materials from vendors shall be changed when the ingredients are changed or technical information is changed. New MSDS's shall be reviewed when received.
- not cover or mark any warning labels used on containers or products received or in use. For transfers to other containers, place labels or legibly mark the containers with the LaRC warning label and the name of the PHM. (NOTE: This marking is not required if the transfer container is used immediately [usually a few minutes] in the process.)

October 3, 2004

**Chapter 3** 

LPR 1710.12

## 3. ACQUISITION, RECEIPT, HANDLING, STORAGE, MARKING, PRESERVATION AND DELIVERY OF POTENTIALLY HAZARDOUS MATERIAL

This chapter describes the procedural requirements for procurement, acquisition, and on site transfer of PHM and MSDS's. PHM may be brought on site and stored or used in facilities after approval by that facility's FSH or designated representative. Procedures for the shipment of PHM off-site are briefly outlined in Chapter 6, "Transportation." Guidelines for the storage of PHM at LaRC are briefly outlined in Chapter 6.

## 3.1 ACQUISITION AND TRANSFER OF POTENTIALLY HAZARDOUS MATERIAL

Refer to Langley Management System (LMS) Procedures CP-4505, 4540, 4703, and 4759.

These procedures shall be followed for all PHM brought on-site including purchasing from commercial sources, through contractor sources, R&D Engineering samples, and commercial product samples. All PHM's brought on-site shall have an MSDS. All MSDS's in the Chemical Material Tracking System (CMTS) shall be submitted to EMT within five working days of receipt of the item. Electronic NASA Langley Form 44 instructions contain additional information.

Use of facility maintenance PHM (solvent, paints, hydraulic fluids, etc.) and cleaning supplies is normally done by on-site contractors. Electronic NASA Langley Form 44 and MSDS's are not required for transfer of maintenance or custodial PHM between the operating site MSDS file and files at individual job sites. These support contractors shall provide appropriate PHM MSDS's for material in use or stored in the facility to FSH's or their representatives.

#### 3.2 IDENTIFICATION OF HAZARDOUS ITEMS BY FEDERAL SUPPLY CLASS

Federal Supply Class (FSC), FED-STD-313C, contains lists identifying hazardous items. Any FSC could contain a hazardous item. The listings in Table I and II of FED-STD-313C are not intended to be inclusive listings of all hazardous items, but to identify the major classes, which contain hazardous items and provide examples of hazardous items in other classes. Contact the LaRC IH Contractor to obtain the most recent version of these Tables.

MSDS's shall be submitted for all items in the FSC-STD-313C, Table I. MSDS's shall be submitted for the hazardous items in FSC-STD-313C not listed in Table I. Some examples of hazardous items in other FSC's are listed in Table II of FSC-STD-313C.

## 3.3 PROCEDURE FOR ACQUISITION, RECEIPT, STORAGE, ISSUE AND DISPOSAL OF HAZARDOUS MATERIALS

## 3.3.1 Acquisition

The following procedures shall be used for the acquisition of PHM. The process for purchasing hazardous material is described within this chapter.

# 3.3.1.1 NASA Purchase Request and Electronic Purchase Request System (EPRS)

Reference LMS-CP-4505, "Prepare Purchase Request (PR) and Supporting Documents."

## 3.3.1.2 Material Handling

Reference LMS-CP-4759, "Receipt, Handling, Storage, Marking, Preservation, and Delivery of Hazardous Materials."

#### 3.3.1.3 NASA Credit Card Order

Reference LMS-CP-4540, "Procurement Purchase Card."

#### 3.3.1.4 NASA Contract Order

Use a NASA Contract Order when supplies are ordered on a regular basis and yearly or periodic needs can be accurately determined. Contracts allow users to take advantage of bulk discounts offered by many companies, without the hazards and costs associated with storage of a large quantity of material. Contact the Chemical Buyer or Contract Administrator prior to preparation of the NASA Langley Form 125, " Purchase Request/Purchase Order (PR/PO)," to set up a contract.

Formal receipt of contract orders is done by the Contract Administrator. When the item is received by the user, send a copy of the packing slip marked as received to LMT Customer Service, Mail Stop 373, for preparation of a NASA Langley Form 131, "Receipt and Inspection Report (Nonstocked Items)." Also, notify the FSH when received so this item can be added to the facility chemical inventory.

For more information, contact the Chemical Commodities Buyer, Office of Procurement.

#### 3.3.1.5 Contractor Purchase

Contractor order, procurement, handling, and disposal of PHM shall be done in accordance with the Statement of Work (SOW) and the terms/conditions of the contract.

## 3.3.1.6 Free Engineering Samples

Many companies will send free samples of materials they normally only sell in large bulk quantities. Use this method if you need only a small amount of material to test for an application and the supplier is willing to send a free sample. NASA Langley Form 44

and an MSDS shall be used for this transaction. Be sure to indicate on line 6 of the NASA Langley Form 44 that the material is a free sample.

Receipt of free engineering samples shall be conducted by Receiving or by the individual, depending on where the item was sent. Notify the FSH (or designated Chemical Inventory Coordinator) when the item is received so it can be added to the facility chemical inventory. For more information contact the LaRC IH Contractor.

## 3.3.2 Transfer of Hazardous Materials Between NASA Langley Research Center Facilities

Reference LMS-CP-4759.

## 3.3.2.1 Transfers to and from the Reuse Facility

Use transfers when turning items into the Reuse Facility or requesting items from the Reuse Facility. The transfer of items requires logging onto the EMT Reuse Facility website and completing the necessary electronic documentation, including a NASA Langley Form 44.

The NASA Langley Form 44 shall automatically be submitted by the CMTS once the online documentation is approved by the Reuse Facility Manager. Turn-in of materials shall be done by facility personnel responsible for hazardous material tracking.

Materials shall be delivered to or picked up from the requesting facility by Reuse Facility Personnel. For more information contact the Reuse Facility Manager.

## 3.3.2.2 Shipping Hazardous Materials to an Off-Site Location

When a hazardous material must be shipped to an off-site location, use NASA Langley Form 52, "Shipping/Transfer Document" or NASA Langley Form 52B, "Shipping Document for Noncontrolled Property (Not to be used for shipping under P.O., Contract, Grant, MOE or Loan," a NASA Langley Form 44, and an MSDS. If the item is a research material, an MSDS shall be prepared prior to delivery of the material to the Shipping Office (Chapter 4).

For more information contact the Shipping Office or the CMTS Administrator.

#### 3.3.2.3 Transfer of Hazardous Materials to and From an Off-site Location

Personally transporting hazardous materials to an outside source is not permitted. If at all possible these products should be mailed off-site. Personally transporting hazardous materials from an outside source is also not permitted. If at all possible, these products should be mailed.

Chapter 4

#### 4. MATERIAL SAFETY DATA SHEETS

This chapter contains information for technical assistance in preparation of MSDS's. The format presented meets basic OSHA guidelines and is in accordance with ANSI 2400.1 - 1993 guidelines. Different countries may have additional technical or procedural requirements for this type of information.

MSDS's are required on all PHM's. A copy of the MSDS for each PHM used in facility research or maintenance operation shall be readily accessible to employees in that facility. Location and set up of MSDS files are the responsibility of FSH's. PHM's include metals, solvents, paints and fiberglass. Review Chapter 3 of "Material Safety Data Sheets and Federal Specifications 313C," for additional information on which materials require MSDS's.

MSDS recordkeeping of facility cleaning and maintenance PHM (including solvents, paints, and hydraulic fluids) is normally done by on-site contractors. These contractor operations can maintain either a central operating site MSDS file or files at individual job sites. These support contractors shall provide appropriate PHM MSDS's for materials in use or stored in the facility to FSH's or their representative, if requested.

For PHM requested by the facility from LaRC supply stock, MSDS information shall be maintained and forwarded by supply personnel when requested by the facility. NASA Langley Form 44B, "Hazardous Materials - Reissue Record" requirements shall be noted in the supply catalog when required.

Trade Secret and Proprietary MSDS's exist and their access and distribution is limited (under OSHA laws) to medical and other selected personnel. In these situations, the LaRC IH Contractor shall be contacted to acquire the necessary information to assist in working with authorized personnel to determine safe use of the materials planned for use. MSDS's so acquired shall be maintained by the LaRC IH Contractor.

#### 4.1 PREPARATION OF MSDS FOR CENTER DEVELOPED MATERIALS

MSDS's shall be prepared to provide basic hazard warning information for materials being transferred between facilities or as operations are scaled up for testing in facilities. MSDS's are required by off-site facilities using the material in other applications. These MSDS's shall be shipped with the material.

All MSDS's prepared shall be reviewed by the LaRC IH Contractor, LaRC Safety Manager, and the PHMC. MSDS's shall be forwarded to the LaRC Safety Manager to start this process.

Copies of the reviewed MSDS's shall be maintained by the LaRC Safety Manager's staff. The twenty-four hour emergency point of contact required by OSHA shall be the Emergency Dispatch Officer at the Fire Department. The Fire Department provides a

telephone service only and shall forward emergency calls to the technical researcher/expert on the item.

#### 4.2 NASA LaRC MSDS LIBRARY

LaRC's EMT shall maintain an electronic library of MSDS's for all known PHM's at the Center through the CMTS. Information from MSDS's along with inventory information collected in the CMTS is used to perform calculations for regulatory reports. These reports are submitted to Federal, State, and local agencies to keep the Center in compliance with environmental as well as health and safety regulations and permits. The procedures for accessing, searching, and adding MSDS's to the MSDS Library are described herein.

## 4.2.1 Accessing and Searching the Library

The Library can be accessed by anyone at the Center through the WWW at the following address:

http://osemant1.larc.nasa.gov/cmts/

Instructions on how to use the Library are on-line or you may contact the CMTS Administrator at the following e-mail address:

#### cmts@larc.nasa.gov

Instructions on how to use the Library is not meant to be a replacement for the Center's MSDS's book, but rather a supplement.

## 4.2.2 Adding MSDS's to the Library

LaRC shall continue to purchase new items to accomplish its research mission. In order to keep the Center's MSDS Library up-to-date, Center personnel shall ensure that MSDS's for new materials are submitted to EMT for entry.

A MSDS shall be submitted for entry to the MSDS Library one of the following ways:

- Fax the MSDS to EMT. Fill in the "To" box on the fax cover with "CMTS Administrator."
- Mail a copy of the MSDS to the CMTS Administrator at MS 418.
- E-mail the web site address, product name, and vendor to the CMTS Administrator at:

#### cmts@larc.nasa.gov.

If Center personnel (civil service or contractor) purchase or otherwise bring a PHM onto the Center and that material's MSDS is not in the Library, that individual shall submit a copy of the MSDS to the EMT within five working days of receipt of the item. If LaRC personnel obtain a more recent or complete version of an MSDS that is in the Library, a copy of the update shall be sent to EMT as soon as possible.

#### 4.3 SCOPE AND APPLICATION

The OSHA Hazard Communication Standard requires that MSDS's shall be prepared for chemicals or mixtures of chemicals that are hazardous as defined in 29 CFR 1910.1200. The policy at NASA LaRC is to prepare MSDS's for all hazardous materials and chemicals, resins, adhesives, powders, fibers, prepreg, towpreg, abrasive materials, ceramic powders, metal alloys, foams, colloids, solutions, oils and lubricants, and gases produced by NASA or on-site contract employees. MSDS's shall be required to transfer materials from the area of origin, or to be shipped off-site for use by another company.

Preparation of an MSDS shall require specific information on the ingredients of a newly developed material. If the researcher or engineer has new, useful or unusual intellectual property, and is uncomfortable about disclosure of such information, they should seek patent protection for their product. Because review of an MSDS will take approximately 30 days, it is necessary for researchers and engineers to anticipate the need for MSDS's prior to shipment of their product off-site. MSDS's shall be prepared in advance for materials that may be needed for technology transfer operations.

This chapter shall be used by persons responsible for developing MSDS's for chemicals produced at NASA-LaRC. This step-by-step guide will aid in the preparation of MSDS's for materials that are invented on-site. Because the information included in an MSDS is from many diverse areas, a team approach shall be used to produce the MSDS, with researchers and engineers collaborating with industrial hygienists, occupational physicians, environmental and fire safety engineers, and the shipping officials who have regulatory knowledge in their appropriate fields. The originator (or responsible researcher) of the material shall have primary responsibility for production and review of the MSDS with contributions made from a number of different individuals. When the final document is completed, a NASA Langley Form 175, "Material Safety Data Sheet Review Request shall be attached to the document and sent for approval to the Chairman of the PHMC.

An MSDS template has been developed to standardize the MSDS's being produced at LaRC. The specific sections of the MSDS are detailed below. Unknown or unavailable information or data shall be indicated as such. Information in this document has been taken from ANSI Z400.1, <u>Standard for the Preparation of Material Safety Data Sheets</u>, and many of the terms and acronyms used here are found in the glossary of that document. The full document contains many useful examples of phrases that may be used in the sections below.

#### 4.4 DETAILED TEMPLATE DESCRIPTIONS

Detailed descriptions of each section of the LaRC MSDS template can be found below.

#### 4.4.1 CENTER IDENTIFICATION

This information shall be provided by the originator or responsible researcher or engineer who developed the material. This section identifies the specific source of the

material at LaRC, identifies a 24-hour contact for emergency information and identifies a technical information contact. If the MSDS is intended for foreign distribution, an indication that the phone numbers are United States phone numbers shall be included.

The format used on the LaRC MSDS template is as follows:

NASA Langley Ro	esearch Center		
	Branch or Org	ganizational Unit	
Mail Stop	- <b>,</b>		
Hampton, VA 23			
<b>Emergency Phon</b>	e: ()	(24-hr contact)	
Information Phon	e: Area code and t	elephone number	of the responsible
researcher of the	material (M-F 9 Al	M to 3 PM EST)	•

#### 4.4.2 SECTION 1: MATERIAL IDENTIFICATION

This information shall be provided by the responsible researcher of the material. This section links the MSDS's to the specific material by listing the trade name, as it appears on the label and a specific product code reference, for example a notebook number, work order number, batch or run number which can be used to provide more specific information on the materials. Synonyms or alternate names shall also be included here, although the trade name shall always be the name listed on the product label.

The format used on the LaRC MSDS template is as follows:

Trade Name: Product Code:

#### 4.4.3 SECTION 2: COMPOSITION

The information on components, Chemical Abstract Service (CAS) Number, and weight percent shall be provided by the responsible researcher of the material. Exposure limit information is provided by the LaRC IH Contractor. This section lists the OSHA hazardous components (as defined in OSHA 29 CFR 1910.1200(g) Appendix A). All ingredients that contribute to the hazards of the material or which otherwise meet the OSHA 29 CFR 1910.1200 criteria shall be identified. If this compound is formed from the chemical reaction of more than one chemical, these ingredients only need to be listed if they are present in the final product in quantities greater than 1percent (0.1 percent for carcinogens).

The format used on the NASA LaRC MSDS template is as follows:

				EXPOSURE LIMITS		
1. 2.	COMPONENT	CAS#	<u>WT %</u>	OSHA PEL	ACGIH TLV	OTHER LIMITS

#### 4.4.4 SECTION 3: HAZARDS IDENTIFICATION/POTENTIAL HEALTH EFFECTS

This section provides information from the LaRC IH Contractor and the responsible researcher on the potential adverse human health effects and symptoms that might result from reasonably foreseeable use or misuse. The format used on the LaRC MSDS template is as follows:

Emergency Overview: List the most significant concerns for emergency

response personnel. It is listed first in this section,

so that it will be easy to find.

Route(s) of Entry: List the probable routes of entry. Include as

applicable: inhalation, absorption through the skin

and eyes, and accidental ingestion.

Signs And Symptoms of

Overexposure:

Immediate or Acute

Effects:

Long Term or Chronic

Effects:

List any known signs or symptoms of overexposure

to materials or components.

List effects that will appear a short time after a single

exposure.

List effects of product or of any hazardous components that may occur over persistent,

prolonged or repeated exposure. Target organ information may also be included here.

Carcinogenicity: Products or components of products, which are

listed as carcinogens or potential carcinogens by OSHA, IARC, NTP or NIOSH, should be specified here. This information is required for components in quantities  $\geq$  0.1 percent. Specify the source of information and class of carcinogen if available.

Reproductive Hazards: Products or components of products, which are,

listed as reproductive hazards or potential reproductive hazards by REPROTEXT, TERIS, REPROTOX or <u>Shepard's Catalog of Teratogenic Effects</u> shall be specified here. Specify source of information and what type of hazard is shown.

#### 4.4.5 SECTION 4: FIRST AID MEASURES

This information is provided by the OHS physician. It shall provide instructions to be taken if accidental exposure requires immediate treatment. It may also include special instructions to medical personnel. This section shall provide information for each applicable route of entry, in lay language, when the results of exposure require immediate treatment (first aid) and when simple measures may be taken before professional medical assistance is available. Include simple remedial measures such as washing exposed area, removing clothing, or removing exposed individuals from the area of exposure if it will lessen the exposure. Also include information on first aid for a specific method of handling as opposed to the toxicity of the material, for example, frostbite from cryogenic liquids. Include any known antidotes that may be administered

by a lay person. Indicate whether immediate medical attention is required and if delayed effects can be expected after exposure.

The format used on the LaRC MSDS template is as follows:

Eyes: Skin:

Inhalation: Ingestion:

Medical Conditions Aggravated by Exposure:

#### 4.4.6 SECTION 5: FIRE FIGHTING MEASURES

This section shall provide basic fire-fighting guidance, including appropriate extinguishing media. It also describes other fire and explosive properties useful for fighting fires involving the material such as flash point and explosive limits. This information shall be provided by the SFAB, SMAO Fire Protection Engineer. The responsible researcher shall provide known or anticipated hazardous products of combustion. The format used on the LaRC MSDS template is as follows:

Flashpoint, <sup>o</sup> F: List the flashpoint of the material as tested by open or

closed cup methods. If the product as a whole has not been tested, state this and list the component with the

lowest flash point in the material.

Method Used: List the flashpoint test used.

Autoignition List the t Temperature, ° F: mixture v Flammable or Calculate

Combustible Classification (NFPA

30):

List the temperature at which a flammable gas or vapor/air mixture will ignite without necessity of a spark or flame. Calculate the class of flammable or combustible liquid using the flashpoint and boiling point of the material. These classifications may be found in NFPA 30 and 29 CFR 1910.1200, OSHA Hazard Communication Standard.

If the item is a flammable solid or gas, state this here. List UEL's and LEL's for the product if available, or for its

Explosive Limits L Upper/Lower: c

components.

List extinguishing media here. The logic shall be similar to that found in the latest edition of the NFPA guide, <u>Fire Protection Guide on Hazardous Materials</u>, Emergency Response Guidebook, DOT P5800.5 and NFPA 325M.

Known or Anticipated Hazardous Products of Combustion:

Extinguishing Media:

Fire Fighting Instructions:

The responsible researcher shall provide this information.

Instructions shall be directed at protecting lives of those in the fire area (including firefighters), and noting unusual impact on the environment and minimizing property loss.

Special environmental warnings, such as toxicity of fire

water runoff, shall be made.

Unusual Fire And **Explosion Hazards:** 

List known or anticipated hazards of flammable and nonflammable materials that initiate or uniquely contribute to the intensity of a fire, such as strong oxidizers (providing fuel), any pyrophoric materials or reaction products, or materials that may form organic peroxides that may be shock or temperature sensitive. Also list the potential for dust explosions, any reactions (with metals for example) which produce flammable gases or vapors, and reactions or conditions with a potential for release of flammable vapors that could cause flash back. Reactivity hazards that enhance the fire and explosion potential shall be listed in this section. Dangerous or explosive reactions with specific chemicals shall be covered in Section 10: Stability and Reactivity.

#### 4.4.7 SECTION 6: ACCIDENTAL RELEASE MEASURES

This section describes actions to be taken to minimize the adverse effects of an accidental spill, leak or release of the material. This information shall be provided by the EMT Environmental Engineer. The responsible researcher shall suggest a neutralizing agent, if known, based on the chemical properties of the material. The format used on the LaRC MSDS template is as follows:

If Material Spills Include information on containment techniques, cleanup or Leaks:

procedures, equipment and other emergency advice relating to

spills and releases. There may be specific reporting requirements to reference information in this section or in

Section 15: Regulatory Information.

Neutralizing This shall be provided by the responsible researcher based on Agent:

the chemical properties of the material. The EMT

Environmental Engineer shall assure that the neutralizing agent

will not create a greater hazard than the product.

#### 4.4.8 SECTION 7: STORAGE AND HANDLING

This information shall be provided by the responsible researcher of the material. It provides information on appropriate practices for safe handling and storage. This section shall be reviewed by the LaRC IH Contractor. The format used on the LaRC MSDS template is as follows:

Storage Precautions:

Emphasize precautions relating to the unique properties of the material. List storage practices that minimize risks from fire for flammable and combustible materials or dangerous reactions with incompatible materials and that minimize the release to the environment. Note or reference specific federal regulatory requirements on the safe storage requirements for the material. Storage temperatures and light conditions shall be listed to extend the life of the material. List hazards of materials that form reactive organic peroxides with time and exposure to air. Hygroscopic materials and specified shelf life shall also be indicated here.

Handling Precautions:

List handling practices that minimize contact between the worker and the material, minimize risks from fire for flammable and combustibles or dangerous reactions with incompatible materials that could cause harm to the worker. Include handling practices such as how to prevent vapor release, the need for a totally enclosed system and safe practices for unloading and moving the material. Include statements about the use of non-sparking tools, explosion proof equipment and grounding when handling flammable materials. List practices that should be followed to prevent dangerous reactions, such as inert blanketing, avoiding oil in equipment used with strong oxidizers, or careful opening of containers that may be under pressure. Include precautions for handling cryogenic or hot materials.

Repair and Maintenance Precautions:

This section shall be used to anticipate the material's use in structural systems, such as using composite materials to fabricate aircraft. Anticipated hazards from dust generated by grinding and drilling, welding fumes generated, or exposure to maintenance personnel shall be listed.

#### 4.4.9 SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

This information shall be provided by the LaRC IH Contractor. It provides information on practices and/or equipment to minimize worker exposure. It also provides guidance on selection of personal protective equipment. The format used on the LaRC MSDS template is as follows:

Eye Protection: Recommend eye and face protection based on the

properties of the materials. For example, corrosive materials would require protective goggles and a face

shield.

Skin Protection: Recommend protective clothing and gloves of the best

barrier material to prevent skin absorption of the material.

Respiratory Identify different types of respiratory protection anticipated Protection: for different conditions and exposure ranges. If air-purifying

respirators are used, the proper cartridge or canister shall be specified. If an air-purifying respirator is not adequate protection, a positive pressure, air-supplied respirator shall

be specified.

This section discusses engineering controls needed to help Engineering Controls:

minimize chemical or physical hazards and to control

exposures during it's anticipated use.

Other Protective

Measures:

As stated.

#### 4.4.10 SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

This information shall be provided by the responsible researcher. This section provides additional data that can be used to help characterize the material and design safe work practices. Any other properties of the material that have been measured shall also be included here. The following characteristics shall appear in this section. Clearly identify if specific characteristics do not apply (NA) or for which data are not available. The format used on the NASA LaRC MSDS template is as follows:

Appearance:

Odor:

Physical State:

pH:

Vapor Pressure, mmHg: Vapor Density, air = 1:

Boiling Point, <sup>o</sup> F:

Freezing/Melting Point (specify which), F:

Specific Gravity,: Solubility in Water:

Other characteristics, which may apply only to certain materials, may be included if known:

Specific heat:

Particle size, microns:

Softening point, ° F:

Evaporation rate, g/min:

Viscosity, dL/q or poise:

Bulk density, g/cm<sup>3</sup>:

Octanol/water partition coefficient:

Saturated vapor concentration:

Molecular weight, g/mol:

Molecular formula:

Fiber areal weight, g/m<sup>2</sup>:

Tg, °C:

Corrosion rate:

Hazardous

Polymerization:

Decomposition temperature:

Volatile organic content, g/L (TEST METHOD):

#### 4.4.11 SECTION 10: STABILITY AND REACTIVITY

This information shall be provided by the responsible researcher based on the material's chemical properties. This section describes the conditions to be avoided or other materials that may cause a reaction which would change the intrinsic stability of the material. The format used on the LaRC MSDS template is as follows:

Stability: Indicate if the material is stable or dangerously

unstable under normal ambient and anticipated storage and handling conditions of temperature and pressure. State if the material will polymerize releasing excess pressure, heat, or creating other hazardous conditions.

State under what conditions the hazardous

polymerization could occur.

Conditions To Avoid: List conditions such as heat, pressure, shock, exposure

to light or air or other physical stresses that might result

in a hazardous situation.

Incompatibility: Address chemicals and other materials that the product

could react with to produce a hazardous situation, for example explosion, release of toxic or flammable materials, liberation of excessive heat or sudden

change of physical state. In determining

incompatibility, consider the materials, containers, and contaminants the product might be exposed to during

transportation, storage and use.

Hazardous List known or anticipated hazardous materials
Decomposition produced as a result of oxidation (except burning),
Products: heating, or reaction with another material, including the

production of flammable and toxic materials.

#### 4.4.12 SECTION 11: TOXICOLOGICAL INFORMATION

This section gives a background of toxicological data on the material or its compounds. If data is not available on the material or it's components, it shall be stated. This information, if available for components of the system, or the product as a whole, shall be provided by the LaRC IH Contractor. If special toxicological tests have been conducted on the material or it's components that are not currently listed on the available national databases this information shall be given to the LaRC IH Contractor.

The format used on the LaRC MSDS template is as follows:

COMPONENT ORAL DERMAL INHALATION OTHER

#### 4.4.13 SECTION 12: ECOLOGICAL INFORMATION

This information, if available for components of the system, or the product as a whole, shall be provided by the EMT Environmental Engineer. This section provides information on the effects the material may have on plants, animals, and its environmental fate. Provide information if the material or it's components have the potential to be toxic in land, water or air. Indicate the potential adverse effect and the species. Indicate if the material or it's components have the potential to persist or bioconcentrate, reaching levels that may have an adverse environmental impact. State if the material or it's components have the unique potential to be harmful to wastewater treatment facilities. If data is not available on the material or it's components, it shall be so stated.

#### 4.4.14 SECTION 13: DISPOSAL CONSIDERATIONS

This section includes information that is relevant to and will assist in determining the proper and permissible waste management options of disposal, recycling or reclamation. The information shall be provided by the EMT Environmental Engineer.

The following information shall be included:

- classification under RCRA, 40 CFR 261,
- US EPA Waste Identification Number and descriptions,
- physical/chemical properties related to disposal option, for example heat value particle size, VOC content,
- special instructions or specific limitations,
- advice that the regulation may also apply to empty containers,
- advice that laws may change,
- advice that state and local regulations are complex and may be different from federal regulations, and
- advice that the owner of the waste has the responsibility for proper disposal.

A disclaimer closure statement may be included as follows:

Chemical additions, processing, or otherwise altering this material may make the waste management information herein incomplete, inaccurate, or otherwise inappropriate. Additionally, state and local requirements for waste disposal may be more restrictive or otherwise different from federal laws and regulations. Consult state and local regulations regarding disposal of this material.

#### 4.4.15 SECTION 14: TRANSPORT INFORMATION

This section provides basic shipping classification information. This information shall be provided by the Shipping Official or EMT Environmental Engineer. The format used on the LaRC MSDS template is as follows:

#### US DOT SHIPPING INFORMATION:

PROPER SHIPPING NAME: UN	HAZARD CLASS:	PG:
REPORTABLE QUANTITY: POSTAL SERVICE:		
IATA SHIPPING INFORMATION:		
PROPER SHIPPING NAME: UN		PG:

OTHER CLASSIFICATIONS: May include classifications/descriptions under International Transportation Regulations, including IMO, ICAO, Transport Canada, ADR and RID.

#### 4.4.16 SECTION 15: REGULATORY INFORMATION

As regulatory databases are cited in the above sections, they shall be included here in a list as they apply to the material. This section shall also be used to provide additional information on regulations affecting materials that are not listed in the previous sections.

US Federal The following regulations shall be searched for the material

Regulations: and it's components: OSHA, FIFRA, TSCA, CERCLA,

SARA Title III, CAA, CWA, SDWA, CPSA, DEA and

FDA/USDA.

US State Regulations: Most states have adopted the OSHA 29 CFR 1910.1200,

but may have additional information requirements. MA, PA, RI and CA require inclusion of state listed substances on the MSDS. PA requires disclosure of nonhazardous ingredients. CA requires listing of VOC's and VT requires

listing of environmental effects.

International The following regulations can be searched for the material Regulations: WHMIS, CEPA, EINECS, MITI, NICAS

#### 4.4.17 SECTION 16: SUPPLEMENTAL INFORMATION

This section is used to list any other information known about the material. Additional information shall also be included in the previous sections where appropriate. The LaRC IH Contractor is responsible for assigning this code after the information in the previous sections is completed. The hazard rating system shall be included in this section using the following format:

HMIS HAZARD RATING SYSTEM: HEALTH = FIRE = REACTIVITY = (scale of 0-4, 4 being most severe)

The responsible researcher shall list his name as the preparer. Other contributors shall also be listed. The date that the MSDS was prepared or revised shall also be included.

Prepared by: Responsible Researcher's Name

Date prepared: Date originally prepared

Revision date: Latest date MSDS was changed (Revisions shall be italicized in body of the document to make changes easy to find.)

#### 4.4.18 SECTION 17: DISCLAIMER

This information is provided by the NASA LaRC Office of Chief Counsel and shall end each MSDS produced at LaRC. The disclaimer statement shall be as follows:

The information and recommendations contained herein are based upon data believed to be correct. However, since much of the information has been received from sources outside NASA Langley Research Center, we cannot guarantee its accuracy or completeness. Health and safety precautions contained within this data sheet may not be adequate for all individuals and/or situations. It is the user's obligation to evaluate and use this data in order to comply with all applicable laws and regulations. Additionally, no guarantee or warranty of any kind, expressed or implied, is made with respect to the information contained herein.

Chapter 5

#### 5. POTENTIALLY HAZARDOUS MATERIAL PERMIT PROCESS

NASA Langley Form 498's issued for PHM are one of the administrative controls available to identify the workers and procedures in use for higher risk PHM operation. The need for and use of NASA Langley Form 498 shall be determined by the FSH and/or the LaRC Safety Manager.

All materials for which OSHA has promulgated a standard based on carcinogenic potential of the material shall be considered for NASA Langley Form 498. Other potential high risk PHM where a NASA Langley Form 498 shall be needed are those materials for which data is not fully available. These include R&D research material where toxicity data is limited (including prepreg material still under research and development and laser dyes). Further information on high hazard material is presented in Chapters 6, 7 and 8.

In areas where PHM technical data is partially or totally unknown (polymers in advanced composites for example), a Laboratory CHP (special form of NASA Langley Form 498) shall be used. The CHP is an OSHA process for control of hazards used in chemical laboratories. CHP's shall be used in all laboratories that routinely synthesize chemicals. Process controls and procedures, rather than PHM specific MSDS's, shall be used to manage the risks from the PHM and their chemical intermediaries.

The PHMC or the LaRC Safety Manager shall also require submission of NASA Langley Form 118, "Safety Permit Request - Hazardous Materials" and issuance of a NASA Langley Form 498 to use any material it deems significantly hazardous.

NASA Langley Form 498's shall be used to standardize procedures and identify training and personnel involved with high-risk operations associated with PHM. Other options permitted for achieving the same risk reduction controls are to use other Committees of functional risk management organizations available at this Center. These include the Systems Operation Committee and/or the Configuration Management Program. The FSH and/or the LaRC Safety Manager can select which of these techniques or combination of programs are best for the situation under consideration. These individuals can disapprove operations or procedures where they consider the risks to be unacceptable and not issue a NASA Langley Form 498.

The FSH or designated representative such as the OFSH, shall complete NASA Langley Form 118 and a NASA Langley Form 66 shall be submitted for each person actively involved in the operation. After completion of any special training or medical requirements, these workers shall be certified as "Chemical Workers" under NASA Langley Form 498.

After review and approval, a NASA Langley Form 498 and a NASA Langley Form 62, "Chemical Worker's Certification Card" shall be issued to each qualified employee. The

worker shall have the card on-hand or readily accessible, as proof of his/her certification, while pertaining applicable tasks. The cards shall be revalidated by the individual's Organizational Unit Manager and the LaRC Safety Manager.

NASA Langley Form 118 shall be prepared by the FSH, the lead test engineer and/or the researcher doing the work. All NASA Langley Form 118's shall be reviewed and resubmitted by the PFSH who has overall responsibility for the entire facility safety program.

# 5.1 SUMMARY OF TOPICS INCLUDED IN NASA LANGLEY FORM 498 ISSUED FOR POTENTIALLY HAZARDOUS MATERIALS

A summary of topics to consider during preparation of NASA Langley Form 118 are as follows:

- · brief description of activity objectives,
- brief description of the PHM or process to be controlled,
  - type and amounts of material present (maximum at site), and
  - amount of material in use during the process (including hazardous material quantity, application rate, flow),
- list of all operators in the controlled area during use of PHM and their operator responsibilities,
- additional training planned for use of PHM named in NASA Langley Form 498.
   Minimum training to meet NASA Langley Form 498 procedures shall be required for each individual named. For example, if LaRC safety videos (such as Gloves for Composite Materials, etc.) are to be required, describe the additional training to be done or required, and
- regulatory requirements: A NASA Langley Form 66 for each civil servant shall be forwarded with NASA Langley Form 118. These forms document training and alert Occupational Health Services (OHS) to possible new medical exam requirements. For each person added after the issuance of a NASA Langley Form 498, forward an additional NASA Langley Form 66. Non-NASA personnel wishing to operate under the NASA Langley Form 498 shall forward equivalent requests through the FSH to the SFAB, SMAO. Personnel shall not operate under the NASA Langley Form 498 until training, medical exams, and LaRC Safety Manager approval have been obtained.

The Safety Operating Plan is the main narrative on how the hazards of the PHM are to be controlled through operational procedures and hazard awareness by workers. The goal of the plan is to describe controls to reduce personnel and facility risks. Narratives submitted with NASA Langley Form 118 shall address the following topics as applicable:

- how the PHM is to be used and controlled. (Note: Use PHM with lower fire or health hazards where possible.)
- planned schedule of operations and estimated frequency of operations. Include comments on weekend operations, and overnight or continuous process schedules, if applicable. These affect risk control procedures. Standard

operations shall involve operators always present during normal day shift unless otherwise noted.

- ventilation system use (including lab hoods exhausting to outside with flow monitoring devices, low flow alarms, etc., as needed). Ventilation alarm device descriptions shall state whether they alarm locally only or to other Center control points (Duty Officer of Fire Department). Responsibilities for calibration of monitoring devices shall be specified.
- procedural controls planned (e.g., Will hazardous gas piping systems be tested
  with inert gases for leaks prior to using toxic or flammable gases? Are gas
  systems to be vented and shut off after each use or remain pressurized? Where
  will low use PHM such as calibration gases or materials be stored [outside for
  hazardous gases] during prolonged no-use periods?).
- personal protective equipment planned for routine operations. (Note: LaRC procedures require that the Fire Department perform all rescue operations in the event of an accident involving personnel.)
- warning alarms and monitoring devices planned for use in control of leak detection procedures (e.g., hydrogen gas alarm, HF gas alarm for Fluorine gas).
   Plans shall include how these alarms will be used to alert operators, other facility personnel, and/or the Fire Department. System shutdown or facility evacuation procedures shall be addressed in conjunction with these alarm set points.
- PHM spill or leak procedures shall be addressed. Minor spills are usually handled by the operators. Specialized training (OSHA required HAZWOPPER 8 hour or longer course) may be required for chemical spills. LPR 8800.1, Chapter 14, "Hazardous Material Spill Control and Contingency Plan," contains spill cleanup information.
- sketches of the operational area, the experimental layout, or piping and valve controls, as applicable.

# 5.2 NASA LANGLEY FORM 498 APPROVALS, DURATION, AND RENEWALS

The PHMC shall determine the approval duration of NASA Langley Form 498. Normally, FSH's or OFSH's shall request approvals for the duration of the R&D activity, if known. Initial approvals shall be for a maximum of one year, and the FSH/OFSH/Project engineer shall reapply for NASA Langley Form 498. Reapplications to continue work shall be submitted to a PHMC representative (normally, the LaRC IH Contractor) at least 30 days before expiration. Maximum renewal periods for existing NASA Langley Form 498's shall be determined by the PHMC and can be up to four years.

Modification to existing NASA Langley Form 498's can be submitted at any time during the issuance. When reviewed and approved, the PHMC shall issue a modified form and a PHMC representative from SFAB, SMAO or the LaRC IH Contractor, shall do initial reviews of new and renewal NASA Langley Form 498s. Final approval of NASA Langley Form 498 shall be conducted by the PHMC and the LaRC Safety Manger.

#### 5.3 WORKER TRAINING AND CERTIFICATION

The NASA Langley Form 498 process shall include a determination of and requirements for PHM worker training and certification including communication, CHP, periodic refresher, and medical surveillance. Worker training and certification shall be conducted in accordance with LPR 1740.6, "Personnel Safety Certification."

# 5.3.1 Potentially Hazardous Material Communication Training

The following information shall be provided or made available to each employee where a PHM is stored or used. This information is considered part of the basic hazard communication program and shall be required for all new employees. NASA personnel shall receive basic hazard communication training within 90 days of being hired and, if needed, through courses provided by SFAB, SMAO. Contractors shall provide an equivalent program for on-site operations.

Employees shall receive this training on LaRC procedures for:

- means of identification of PHM's (i.e., labeling and posting, Chapter 6),
- health hazard data,
- fire, explosion, and reactivity data,
- precautions for safe use, handling, storage, and disposal,
- required protective clothing and equipment, and
- · emergency and first aid procedures.

The MSDS's shall be used as a primary source for this information. Personnel shall be cognizant of this information prior to actually handling the material.

# 5.3.2 Chemical Hygiene Plan Training

Training for laboratory workers operating under a CHP is in addition to the preceding. All workers involved in processes conducted under the CHP shall be familiar with the basic NASA Langley Form 498 procedures for their operation and/or facility. This training shall be the responsibility of the designated CHO. Support shall be provided by the LaRC IH Contractor as appropriate.

#### 5.3.3 Periodic Refresher Training

Periodic refresher training shall be required if the hazardous materials change or the processes generating hazardous materials change. This training shall be the responsibility of the FSH and/or the CHO, with SFAB, SMAO, assistance as needed.

#### 5.4 MEDICAL SURVEILLANCE

Medical monitoring of personnel at risk from exposure to PHM shall be done by the OHS personnel at the Occupational Medical Center (OMC), 10 West Taylor Street, Facility 1149. The requirements for medical surveillance are identified by Occupational Medical Examination Protocols (OMEP's) determined by the OHS physician and

assessments of risk by the LaRC Safety Manager and his/her staff through periodic audits or special surveys of workplaces requested by FSH's. Other site or OSHA requirements, such as those determined in past Labor Management agreements or substance specific OSHA standards, shall also be used in determining the need for, and procedures in, examinations. The LaRC IH Contractor shall normally perform all assessments of site PHM health risks and report these to FSH's and the LaRC Safety Manager.

FSH's and their designated representatives shall establish procedures for periodic review of their at risk worker population for the use of PHM. At-risk workers shall be identified to the OMC at the time of initial assignment to work with PHM through the use of NASA Langley Form 66. Pre-certification and annual examinations, as well as examinations required due to exposure shall be scheduled and conducted by the OMC in accordance with the applicable OMEP. The completed NASA Langley Form 66's shall be maintained in individual medical records at the OMC.

The determination of the need for periodic medical surveillance of workers shall depend on several factors, including the PHM in use, toxicity, manner and duration of use, and potential routes of entry into workers. Depending on the nature of the hazards, medical surveillance may be recommended. FSH's shall request assistance from the LaRC IH Contractor in the risk assessments. Occasionally, such as in the use of R&D mutagenic material, additional input from the OHS physician may be needed to determine OMEP needs.

FSH's shall identify temporary or transient personnel who periodically come into their facility to work with PHM. For example, an Engineer may come into their laboratory for five days per month over six months to do "hands-on" work in PHM R&D of a new process. If the risks warrant clinical monitoring, these temporary or non-civil service personnel shall be identified to the OMC using NASA Langley Form 66 or equivalent contractor forms. As a general rule, if other workers receive clinical examinations for exposure for their daily work with low to moderately toxic material, these temporary workers shall also be referred to the OMC for monitoring if they receive more than one month's (20 days) exposure in a year.

All workers named on NASA Langley Form 498 are considered Chemical Workers. Specific clinical examinations for Chemical Workers shall be determined by the OHS physician. Procedures for use of NASA Langley Form 498, NASA Langley Form 62, and clinical examinations are presented in LPR 1740.6. Chemical Workers are the individuals who physically use the material or are, or could be, involved in the permitted operations. Administration and management personnel shall not be considered unless they actually work with the material named.

Reviews or updates to identify personnel needing, or no longer needing, PHM related clinical examinations shall be conducted by FSH's after consultation with facility personnel, as circumstances warrant. These clinical examination listing updates shall be conducted during periodic audits (industrial hygiene audits) of facility operations.

The OHS OMC shall, as circumstances warrant, notify the LaRC Safety Manager and FSH's on trends seen in the worker population monitored through its OMEP program.

Clinical examinations required because of workplace exposures to PHM can be either recommended or mandatory by law. If medical surveillance is recommended and the employee declines to participate, the OHO shall obtain a statement which shall be included in the employee's medical records. The statement shall indicate that the employee understands the risk involved by declining to participate in the surveillance program. The LaRC Safety Manager and FSH's shall be notified concerning trends or individuals declining to participate.

If the medical examination is mandatory by law, appropriate personnel (including supervisors and FSH's) shall be notified if the individual fails to complete medical monitoring examinations for the workplace PHM exposure.

Chapter 6

#### 6. USE AND HANDLING OF POTENTIALLY HAZARDOUS MATERIALS

Prior to initial acquisition or transfer of PHM, FSH's shall make the initial decision on the use of a particular PHM or PHM process in their facility, the amount to be stored in the facility, and the initial assessments for further safety and process control measures. In cases where PHM pose a significant hazard because of their toxicity, flammability, or other potentially hazardous properties, control procedures and other operational details shall be documented and approved through the NASA Langley Form 498 process. The NASA Langley Form 498 process is discussed in Chapter 5.

Additionally, safety assistance can also be provided by the LaRC Safety Manager, his/her staff, the PHMC, other LaRC committees, and other technical area experts.

# 6.1 LABORATORY OPERATIONS AND PRODUCTION OF POTENTIALLY HAZARDOUS MATERIALS

Laboratory operations and production of PHM includes chemical synthesis in laboratories and the transfer of test chemicals.

# 6.1.1 Chemical Synthesis in Laboratories

Production or synthesis of chemicals and their intermediaries are usually involved processes. Laboratories performing these processes shall have a CHP. The NASA Langley Form 498 process shall be used for each laboratory CHP. Laboratories operating under a CHP shall not be required to have MSDS for each chemical intermediary involved in the chemical process. Federal law requires annual review of the chemical hygiene plan.

# 6.1.2 Transfer of Test Chemicals

On-site operations that produce test specimens of PHM's for use in other facilities and/or special projects shall provide MSDS's for use by other personnel working with the material. The LaRC MSDS template is in Chapter 4. MSDS's produced shall be forwarded to the LaRC IH Contractor for review and submittal to the PHMC and LaRC Safety Manager.

#### 6.2 WARNING LABELS AND HAZARD INFORMATION

Warning labels and hazard information shall be required for PHM.

#### **6.2.1 Potentially Hazardous Materials Labels**

The material or its container shall be clearly labeled to identify the material (chemical name or trade name) and to provide precautionary statements required by regulatory agencies or LaRC. The material or its container shall bear the diamond symbol of the National Fire Protection Association (NFPA) in accordance with NFPA Handbook 704, "Standard System for the Identification of Hazardous Materials for Emergency

Response," (Figure 6.1). This symbol indicates the severity of hazard on a numerical scale of 0 to 4, and type of hazard (health, flammability or reactivity) according to a color code. The ranking of severity of the health hazard is based upon acute exposures, and therefore, may not adequately reflect the actual hazard associated with chronic exposures to relatively small quantities of the material. Any material subject to a specific OSHA labeling standard shall be labeled in accordance with those requirements in addition to those given above.

LaRC shall use the NFPA diamond as a warning symbol to increase worker awareness of hazardous materials. This diamond label and the type of material shall be placed on all transfer containers of hazardous materials that do not have labels meeting the OSHA Hazard Communication standard. For example, a laboratory squeeze bottle used to hold the cleaning solvent methyl ethyl ketone will have an NFPA diamond label with numbering for HEALTH = 1, FLAMMABILITY = 3, and REACTIVITY = 0.

Figure 6.1 shows the diamond label and the rationale for assigning codes. Codes for several chemicals are found in the NFPA Code 704. Assistance on assigning these codes can be obtained from the LaRC IH Contractor, SFAB, SMAO. The diamond code information shall be entered on NASA Langley Form 44, when the request for PHM's is submitted.

All PHM used and stored at the Center shall have a CMTS label with its inventory record number. Detailed information on CMTS labels is available on-line at:

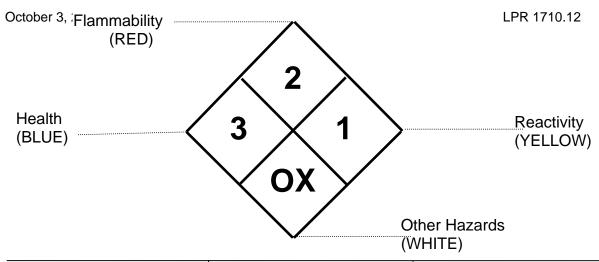
# http://osemant1.larc.nasa.gov/cmts/instruct/

# **6.2.2 Hazard Survey Information**

The NFPA diamond symbol is intended to increase worker awareness of the presence of PHM's. The actual hazard from a material depends on how it is used. Periodic audits and surveys shall be conducted by safety and industrial hygiene personnel to determine actual health hazards from hazardous material operations. The results of these audits shall be reported back to the facilities. Workers can request information on past surveys by contacting their supervisors, LaRC Safety Manager or the LaRC IH Contractor.

# 6.3 STORAGE AND POSTING AREAS WITH POTENTIALLY HAZARDOUS MATERIAL

PHM, particularly compressed gases and flammables or combustibles, shall be stored in accordance with Figures 6.2, 6.3 and 6.4. Before use, planning of new operations shall incorporate all statutory requirements as promulgated



Identification of Health Hazards Color Code: BLUE		Identification of Flammability Color Code: RED		Identification of Reactivity Color Code: YELLOW	
	Type of Possible Injury	Susce	ptibility of Materials to Burning	Susc	ceptibility to Release of Energy
Signal		Signal		Signal	
4	Materials, which on very short exposure could cause death or major residual injury even though prompt medical treatment, is given.	4	Materials, which will rapidly or completely, vaporized at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn	4	Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.
3	Materials, which on short exposure could cause serious temporary or residual injury even though prompt medical treatment, is given.	3	Liquids and solids that can be ignited under almost all tambient temperature conditions.	3	Materials which in themselves are capable of detonation or explosive reaction, but require a strong initiating source or which must be heated under confinement before initiating, or which react explosively with water.
2	Materials, which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment, is given.	2	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.	2	Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also materials, which may react violently with, water or which may form potentially explosive mixtures with water.
1	Materials, which on exposure could cause irritation but only minor residual injury, even if no treatment is given.	1	Materials that must be preheated before ignition can occur.	1	Materials, which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures, or which may react with water with some, release of energy, but not violently.
0	Materials, which on exposure under fire conditions, would offer no hazard beyond that of ordinary combustible materials.	0	Materials that will not burn.	0	Materials, which in themselves are normally, stable, even under fire exposure conditions, and which are not reactive with water.

Other Hazards - Color Code: WHITE

Ox - Oxidizer

W - Use no water

Figure 6.1, National Fire Protection Association Symbols.

by OSHA and any other national consensus standards. These include recommendations of the NFPA, Compressed Gas Association, and American National Standards Institute.

Guidelines for storage of flammable materials are given in this chapter. Contact the LaRC Safety Manager or the LaRC Fire Chief if assistance is needed in determining flammable storage needs and requirements.

# **6.3.1 Storage of Potentially Hazardous Materials**

The requirements for storage of PHM in a facility, or adjacent to a facility, are to minimize risks in the event of fire or accident. Requirements for gases are detailed in Chapter 8. Material quality storage requirements, such as use of refrigerated storage to prolong the quality of the substance, are not considered or detailed in this chapter. For storage of environmentally regulated hazardous wastes, consult LPR 8800.1.

Fire codes for the storage of flammable materials in facilities have been incorporated into OSHA standards. These OSHA mandatory requirements are included in this chapter. For assistance in interpreting these laws, contact the LaRC Safety Manger or LaRC Fire Chief.

# 6.3.2 Flammable and Combustible Liquids Storage

This section applies to the storage of flammable or combustible liquids in drums or other containers not exceeding 60 gallons individual capacity and portable tanks not exceeding 660 gallons individual capacity. For further interpretation, contact SFAB, SMAO.

# 6.3.2.1 Design and Capacity of Containers

Only approved containers and portable tanks shall be used. Metal containers and portable tanks meeting the requirements of and containing products authorized by Department of Transportation (DOT) 49 CFR, Transportation, Chapter 1, Research and Special Programs Administration, Department of Transportation (regulations issued by the Hazardous Materials Regulations Board, Department of Transportation), shall be deemed to be acceptable. The LaRC Fire Chief shall be available to provide guidance in these areas.

# 6.3.3 Suggested PHM Shelf Storage Pattern

Figures 6.2, Suggested Shelf Storage Pattern, 6.3, Partial List of Incompatible Compounds (Toxic Hazards), and 6.4, List of Incompatible Chemicals, contain information obtained from a NASA Course on Laboratory Safety and Health. No current regulatory requirements exist for storage lockers, however, the data presented are suggested for use to help avoid storing incompatible materials on the same or adjacent shelves.

INORGANIC	ORGANIC
INORGANIC # 10	ORGANIC # 2
SULFUR, PHOSPHORUS, ARSENIC,	ALCOHOLS, GLYCOLS, Etc.
PHOSPHORUS PENTOXIDE	(Store flammables in dedicated cabinet)
INORGANIC # 2	ORGANIC # 3
HALIDES, SULFATES, SULFITES,	HYDROCARBONS, ESTERS, Etc.
THIOSULFATES, PHOSPHATES, Etc.	(Store flammables in a dedicated cabinet)
INORGANIC # 3	ORGANIC # 4
AMIDES, NITRATES. (Not	ETHERS, KETONES, Etc.
AMMONIUM NITRATE).	(Store flammables in a dedicated cabinet)
Nitrates, Etc.	,
INORGANIC # 1	ORGANIC # 5
METALS AND HYDRIDES	EPOXY COMPOUNDS, ISOCYANATES
(Store away from water)	·
INORGANIC # 4	ORGANIC # 7
HYDROXIDES, OXIDES, SILICATES, Etc.	SULFIDES, POLYSULFIDES, Etc.
INORGANIC # 7	ORGANIC # 8
ARSENATES, CYANIDES, Etc.	PHENOL, CRESOLS
(Store above acids)	·
INORGANIC # 5	ORGANIC # 6
SULFIDES, SELENIDES, PHOSPHIDES,	PEROXIDES, AZIDES, Etc.
CARBIDES, NITRIDES, Etc.	
INORGANIC # 8	ORGANIC # 1
BORATES, CHROMATES,	ACIDS, ANHYDRIDES, PERACIDS, Etc.
MANGANATES,	
PERMANGANATES, Etc.	
INORGANIC # 6	
CHLORATES, PERCHLORATES,	MISCELLANEOUS
CHLORITES, PERCHLORIC ACID,	
PEROXIDE, Etc.	
INORGANIC # 9	
ACIDS, except NITRIC	MISCELLANEOUS
(Acids are best stored in dedicated	(Nitric Acid)
cabinets)	

Figure 6.2, Suggested Shelf Storage Pattern

Arsenical Materials	Any Reducing Agent	Arsine
Azides	Acids	Hydrogen Azide
Cyanides	Acids	Hydrogen Cyanide
Hypochlorites		Chlorine or Hypochlorous Acid
Nitrates	Sulfuric Acid	Nitrogen Dioxide
Nitric Acid	Copper, Brass, Heavy Metals	Nitrogen Dioxide
Nitrites	Acids	Nitrous Fumes
Phosphorus	Caustic Alkalis/Reducers	Phosphine
Selenides	Reducers	Hydrogen Selenide
Sulfides	Acids	Hydrogen Sulfide
Tellurides	Reducers	Hydrogen Telluride

Figure 6.3, Partial List of Incompatible Chemicals (Toxic Hazards)

Substances in the left hand column shall be stored and handled so that they cannot possibly accidentally contact corresponding substances in the center column, as toxic materials (right hand column) would be produced.

Chemical	Potentially Incompatible Chemicals/Materials/Conditions
Acetic acid	Chromic acid, nitric acid, perchloric acid, hydroxyl-containing compounds, ethylene glycol, peroxides, and permanganates
Acetone	Concentrated nitric, sulfuric, perchloric, and chromic acid mixtures, and certain plastic materials
Acetylene	Chlorine, bromine, copper, silver, brass (red), flourine, mercury, and oxygen
Ammonium nitrate	Acids, metal powders, flammable liquids, chlorates, nitrates, sulfur, finely divided organics, or combustibles
Ammonium hydroxide	Acids
Ammonium iodine	Acids and oxidizing agents
Ammonium sulfide	Acids
Arsenical materials	Any reducing agent
Bromine	Ammonia, acetylene, butadiene, butane, and other petroleum gases; hydrogen; sodium carbide; turpentine; benzene; and finely divided metals
Carbon, activated	Calcium hypchlorite and ruthenium tetroxide
Carbon tetrachloride	Sodium
Chlorates	Ammonium salts, acids, metal powders, sulfur, finely divided organics, or combustibles
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, benzene, finely divided metals, and turpentine
Chromic acid	Acetic acid, acetone, naphthalene, camphor, gylcerine, turpentine, alcohol, and most flammable organic compounds
Copper	Acetylene of hydrogen peroxide
Cyanides	Acids
Diethyl ether	Nitric acid (concentrated and fuming) and other strong oxidizing agents (dichromate, permanganate), heat, or aluminum
Flammable liquids	Ammonium nitrate, chromatic acid, hydrogen peroxide, nitric acid, sodium peroxide, and halogens

Figure 6.4, List of Incompatible Chemicals (page 1 of 2)

Chemical	Potentially Incompatible Chemicals/Materials/Conditions
Hydrochloric acid	Bases or manganese dioxide
Hydrocyanic acid	Nitric acid or alkalis
Hydrogen peroxide	Copper, chromium iron, most metals or their salts, and flammable liquid, combustible materials, aniline, and nitromethane
Hydrofluoric acid (anhydrous)	Ammonia, aqueous, or anhydrous
Hydrogen sulfide	Fuming nitric acid, oxidizing gases, heat, and most common metals
Hydrocarbons (benzene, butane, propane, gasoline, turpentine, etc.)	Flourine, chlorine, bromine, chromic acid, and sodium peroxide
Mercury	Acetylene, fulminic acid, ammonia, and concentrated nitric acid
Methyl isobutyl ketone	Nitric acid (concentrated and fuming), dichromate, and (hexane) permanganate
Nitric acid (conc.)	Acetic acid, aniline, chromic acid, Hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, nitratable substances such as organic compounds, including diethyl ether and methyl ketone (hexane), and bases
Oxygen	Oils, grease, hydrogen, flammable liquids, solids, or gases
Oxalic acid	Silver and mercury
Perchloric acid	Acetic anhydride, acetone, alcohol, bismuth and its alloys, charcoal, paper, wood, bases, or organic compounds
Potassium chlorate	Acids and organic compounds
Potassium perchlorate	Acids and organic compounds
Potassium permanganate	Glycerine, ethylene glycol, benzaldehyde, and sulfuric acid
Sodium carbide, acetylene	Water (also see acetylene, which is liberated from sodium carbide on exposure to moisture)
Sodium hydroxide	Acids, organic materials, most common metals, and water
Sodium nitrate	Ammonium nitrate and other ammonium salts
Sodium peroxide	Any oxidizable substance, such as ethanol, methanol, glacial acetic acid, acetic anhydride, benzaidehyde, carbon disulfide, glycerine, ethylene glycol, ethyl acetate, methyl acetate, and furfural
Sulfuric acid	Chlorates, perchlorates, permanganates, water, and bases
Strong bases	Strong acids, organic materials, water and most common metals

Figure 6.4, List of Incompatible Chemicals (page 2 of 2)

# 6.3.4 Storage Time Limits of Peroxidizable Compounds

Some chemicals form peroxides upon prolonged storage and/or contact with air. The peroxide formed may be explosive or highly reactive, and could detonate by twisting the container cap. A list of some of these chemicals is at Figure 6.5, Storage Time Limits of Peroxidizable Compounds. If crystals are noticed, exercise extreme caution and notify the FSH and LaRC Safety Manager for assistance as soon as possible.

#### 6.4 TRANSPORTATION OF POTENTIALLY HAZARDOUS MATERIAL

Specific requirements for off- and on-site transport of PHM are detailed below:

# **6.4.1 PHM Transportation Off-Site**

PHM's shall not be introduced into interstate commerce unless in full compliance with applicable regulations of DOT 49 CFR, Subchapter C, Hazardous Materials Regulations, Parts 171-177. For example, materials containing cyanides shall not be transported in vehicles containing acids.

Contact the LMT for assistance on shipment and for restrictions on movement of PHM off-site. LMT personnel can assist in authorized type of shipments (e.g. pounds of PHM that are air transportable, performance oriented packaging requirements, PHM transportation package, vehicle placarding).

PHM transported off-site shall be accompanied by a NASA Langley Form 44 and the appropriate MSDS. The NASA Langley Form 44 is used to track LaRC hazardous material.

Shipments of minor (less than 10 gram) quantities of PHM laboratory samples for offsite testing do not require a NASA Langley Form 44. The package label for these items shall clearly identify the name, address, and phone number of the individual knowledgeable about the test specimen, a brief description of the samples, and date shipped in order to meet Federal guidelines for shipment of laboratory samples as defined in DOT 46 CFR, Shipping. Check for other PHM limits on quantity, transportation methods, and packaging that apply to the shipment.

Any person transporting PHM off-site is subject to the motor vehicle laws of the Federal Government and the Commonwealth of Virginia. Current laws require certain classes of motor vehicle operators to have Commercial Driver's Licenses for transport of PHM.

#### **6.4.2 PHM Transportation On-Site**

On-site transportation of PHM shall be conducted by personnel trained in hazardous material transportation. Contact the LMT for assistance in hazardous material transfer.

# RED LABEL - PEROXIDE HAZARD ON STORAGE DISCARD AFTER THREE MONTHS

isopropyl ether divinyl acetylene vinylidene chloride potassium metal sodium amide

# YELLOW LABEL - PEROXIDE HAZARD ON CONCENTRATION DISCARD AFTER ONE YEAR

diethyl ether dicyclopentadicene

tetrahydrofuran diacetylene

dioxane methyl acetylene

acetal cumene

methyl isobutyl ketone tetrahydronaphthalene (TetraUn)

ethylene glycol dimethyl cyclohexene

ether (glyme)

vinyl ethers methylcyclopentane

# YELLOW LABEL - HAZARDOUS DUE TO PEROXIDE INITIATION OF POLYMERIZATION\* DISCARD AFTER ONE YEAR

methyl methacrytate chlorotrifluoroethylene

styrene vinyl acetylene acrylic acid vinyl acetate acrylonitrile vinyl chloride butadiene- vinyl pyridine tetrafluoroethylene chloroprene

From H. L. Jackson, W. B. McCormack, C. S. Rondestvedt, K. C. Smeltz, and I. E. Viele: "Safety in the Chemical Laboratory. LXI: Control of Peroxidizable Compounds." *J Chem. Educ.* 47(3): A176 (March, 1970).

Figure 6.5, Storage Time Limits of Peroxidizable Compounds

<sup>\*</sup>Under conditions of storage in the liquid state, the peroxide-forming potential increases and certain of these monomers (especially butadiene, chloroprene, and tetrafluorethylene) should then be considered as A-list compounds.

NASA personnel without a Commercial Drivers License may use NASA vehicles for limited on-site transfer of PHM. An example would be an emergency transfer of hydraulic fluid from stock or another on-site facility to support pump repair work for a wind tunnel.

# 6.5 EXCESS PHM, ACCIDENTS INVOLVING PHM, AND DISPOSAL OF WASTE PHM

Information on various other topics associated with storage, excess turn in, spills, documenting (i.e. MSDS) information of new materials, OSHA carcinogens, hazardous gases, etc., is outlined in more detail in other chapters of this LPR, in the LaRC Safety Manual, or in LPR 8800.1. Additional general procedures are included herein.

Use of alternative material, ventilation, and personnel protective equipment shall be considered in all processes. Whenever possible, less hazardous material shall be substituted first in processes. If substitution is not possible, process ventilation shall be used to minimize hazards. Ventilation design guidelines, as found in the American Conference of Governmental Industrial Hygienists Ventilation Manual, shall be used. As a last resort, personnel protective equipment shall be relied on to minimize risks from PHM. Procedures for obtaining individual personnel protective equipment (gloves, eye wear, respirators, etc.) are presented in LPR 1710.4, "Personnel Protection - Clothing and Equipment." FSH's can contact the LaRC IH Contractor for recommendations.

Transportation of PHM has been briefly presented earlier in this chapter. Personnel are expected to follow appropriate Federal and Commonwealth of Virginia PHM transportation regulations.

#### 6.5.1 Excess PHM

If excess PHM drawn from stock is in original condition, it shall be sent to the Reuse Facility to be available for use by other Center personnel. Also, to minimize fire and other risks in the event of a facility accident, excess material shall be returned to the Reuse Facility in lieu of storing it at the facility.

Reuse Center procedures shall be followed for turn-in of excess PHM

#### 6.5.2 Reuse Facility

Excess PHM, after operations are completed shall be turned in to the Reuse Facility through CMTS or turned in for disposal using the disposal forms. Prolonged storage of excess material on-site wastes storage space and can result in waste of quality materials by keeping them past useful shelf storage life. PHM generating waste in processes shall be subject to environmental regulations and site procedures, which are presented in LPR 8800.1.

The Reuse Facility is operated by EMT as a service to the Center. Civil servants and on-site contractors can request materials from or turn materials in to the Reuse Facility on-line at:

# http://osemant1.larc.nasa.gov/cmts/reuse

There is no cost to withdraw chemicals from the Reuse Facility and materials will be delivered to the facility. Policies and procedures for the Reuse Facility can also be found through website listed above.

# 6.5.3 Accidents, Spills, and First Aid Involving PHM

All accidents involving PHM, no matter how small, shall be reported to the Head, EMT and the FSH. Personnel using the material shall be responsible for clean up of minor spills in their work area. Minor accidents, when reported, can lead to a recognition of potential trends and identification of needs for better equipment or procedures. For example, a minor break and splash of PHM from a beaker in a lab hood could lead to the identification of a need for lab chemical splash barriers.

Establishing accident and first aid procedures is an integral part of planning for the use of PHM. It is the responsibility of the user to effectively contain PHM in event of a minor spill and to perform cleanup operations. Consultation with EMT in developing emergency procedures shall be required. All spills of PHM shall be reported to EMT. PHM's are to be deleted from inventory using the CMTS.

Professional First Aid service is available at the LaRC OMC, 10 West Taylor Street (Facility 1149), 7:00 a.m. – 3:30 p.m., Monday through Friday. On-site ambulance service can be obtained anytime by calling 911.

Preplanning for accidents involving PHM shall always be required. Specialized training (OSHA HAZWOPPER 8 hour or longer course) may be required for chemical leaks of PHM over one pint or one pound in size depending upon the situation involved. Spill clean up information and procedures to request assistance for spills beyond facility capabilities shall be in accordance with LPR 8800.1, Chapter 14, "Hazardous Material Spill Control and Contingency Plan," and on-line at:

http://osemant1.larc.nasa.gov/

#### 6.5.4 Waste PHM

Waste PHM disposal shall be in accordance with Federal, State, and local regulations, and LaRC procedures presented in LPR 8800.1. Contact EMT for more information or the EMT web page listed above.

**Chapter 7** 

# 7. GENERAL TECHNICAL INFORMATION ON TYPES OF POTENTIALLY HAZARDOUS MATERIALS (EXCLUDING GASES)

This chapter provides general technical data to assist LaRC employees in recognizing and controlling health and safety related problems that may arise from use of PHM's. It contains information on solvents, acids, bases, OSHA carcinogens, and so forth. Information on selected gases is in Chapter 8.

Additional information on PHM can be found in the MSDS for items in use. This is typically the first reference for PHM users in facilities. Prior to use or acquisition, site personnel shall check existing databases on PHM to include current MSDS's on the materials proposed for use, or other existing facility process information. The Center has an on-line MSDS Library at:

# http://osemant1.larc.nasa.gov/cmts/

Assistance in interpreting information can be obtained from EMT the LaRC IH Contractor, and the PHMC.

For R&D operations, additional review on the reaction products during the process, or possible accidental reaction process hazards, shall be performed prior to starting the operation. For example, work with gallium arsenide semiconductor chips may result in small releases of lethal arsine gas with little or no associated odor. Cyanide compounds used in metal etching or photographic processes can form lethal cyanide gas if a spill occurs with acids and cyanide compounds present. Also, work with hydrogen gases involves high flammability risks. All of these are examples of PHM with risks controllable through the use of training, process control (ventilation - fume hoods), gas leak testing and monitoring devices when these measures are put in place and used with PHM operations.

#### 7.1 GENERAL INFORMATION ON CLASSES OF PHM

#### 7.1.1 Flammable Liquids

The handling of solvents requires trained personnel. Because of the nature and variety of these chemicals, poisoning, evaporation, fire, and explosion hazards exist. Incompatible solvents shall not be stored together and all containers should be properly sealed and kept in suitable areas. (Guidelines for storage are in Chapter 6.) Protective clothing shall be worn and the laboratory or use area shall be equipped with safety equipment commensurate with the hazards of the solvent. It may be necessary to also have a spill cleanup kit on hand and readily available to handle small spills (Chapter 6). Some operations involving the handling of solvents require shielding, special hoods or special protective clothing such as gloves, aprons, face shields, goggles, coats, or other

special garments. Information or assistance on the selection of these devices can be obtained from the FSH or by contacting SFAB, SMAO or the LaRC IH Contractor.

#### 7.1.2 Acids and Bases

The handling of acids, bases, corrosives, and toxic chemicals demands adequately trained personnel. Other persons shall not be granted access to the stores or permitted to handle such materials. Because of the nature and variety of these chemicals, their hazards range from poisoning, burning, and gassing through explosion. Care shall be exercised to assure that incompatible chemicals are not stored together. All containers shall be properly sealed and kept in appropriate storage areas. Suitable protective clothing shall be worn and the laboratory shall be equipped with safety equipment commensurate with the hazards of the acid or base, such as an eyewash station, a safety shower, and a fume hood. It shall be required to have a spill cleanup kit on hand and readily available to neutralize small spills. Most chemicals of this class are capable of inflicting severe burns when spilled on skin or clothing. Pending medical treatment, initial first aid for every chemical burn is to wash off the chemical by flooding the burned area with very large amounts of water as quickly as possible. This is the only method for limiting the severity of the burn, and the loss of even a few seconds can be vital. Following complete washing, the burn should be covered with a clean, preferably sterile, cloth or sheet, and the victim should be taken to a physician. No ointment, salve, grease, stimulant or other remedy shall be used without the physician's advice. Dial 911 for medical assistance. Some operations involving the handling of this class of chemicals require shielding, special hoods, or special protective clothing such as gloves, aprons, face shields, goggles, coats, or other special garments.

#### **7.1.3 Acids**

As a group, acids are highly reactive. This reactivity adds to their usefulness but it also demands that laboratory spills be given special attention. Three factors should be remembered when considering methods to clean up minor acid spills:

- reactivity with water,
- corrosiveness of the chemical and its decomposition products, and
- irritability of the chemical and its decomposition products.

Problems associated with these factors can be easily solved with common sense and general laboratory safety.

Water **shall not** be used on most concentrated acid spills unless the water can be delivered in deluge quantities. Most concentrated acids react vigorously with water, producing corrosive products. In addition, the exothermic reaction will cause increased vaporization of the reagent, which may have a pungent irritating odor even under the best of ventilation conditions. Reagent spills shall first be absorbed with the appropriate spill cleanup kit. The damp mixture can then be scraped up with a plastic, ceramic, or metal scoop. Successful use of this technique requires that the spill cleanup kit be readily accessible. EMT shall be contacted for disposal of the cleanup material.

As in the handling of most chemical spills, safety glasses and rubber gloves are needed to safely clean up acid spills. Gloves do not permit prolonged contact but they offer adequate protection for the removal of most spills. Splashes on the skin or in the eyes should be rinsed immediately with a heavy flow of water. Clothing splashed with acids shall be removed and washed before reuse.

**Avoid acid mists in air.** Small spills, which occur in a clear open area, such as the floor or the center of a laboratory bench, can be cleaned by personnel with only a brief exposure to mists. Other spills may be larger or occur in an inconvenient spot with poor ventilation, causing higher exposures and necessitating use of a self-contained respiratory device. This equipment consists of a facemask and a cylinder of air, which can be carried or strapped to the belt or to a shoulder harness.

The occurrence and effects of spills can be minimized by observing a few general precautions:

- Limit the size of reagent bottles in the laboratory. Generally, only a one-month supply of chemicals shall be kept in the laboratory area. Larger quantities shall be kept in approved facility storage vaults.
- Leave adequate headspace in bottles.
- Do not store reagents in a warm spot.
- Keep the bottles in a tray, preferably ceramic or glass lined.
- Keep an acid spill kit.
- Do not use water to fight a fire involving acids. Use a dry chemical or CO<sub>2</sub>
  extinguisher. Water can be used for small spill amounts if the water is delivered
  in deluge quantities.
- Use approved bottle carriers when necessary to transport chemicals.

# **7.1.4 Bases**

The major hazard in the use of bases is their corrosive action on tissue. Severe, painful tissue damage can rapidly result from acute exposures in which significant amounts of bases are inhaled, splashed on the skin, or swallowed.

Contact with the skin or eyes are the most common hazard. Unlike inhalation exposures, contact injuries occur frequently in the laboratory. Only small amounts of concentrated bases are needed to cause damage, which may range from annoying irritation to deep flesh burns and permanent visual impairment. Mist or spray, which is too light to cause a skin break, may cause dermatitis. If the exposure is constant, more serious skin problems may develop, requiring prolonged medical treatment.

Workers shall be cautioned to check themselves over thoroughly after working around bases to ensure that no clothing or skin has been attacked. There is no warning sting with bases, as with acids, and an unattended burn can make considerable headway before it is noticed.

The most important aspect of any spill is the prompt removal of the chemical, which contacts the skin or eyes. Concentrated bases are not easily rinsed from the skin and continuous flushing with water is needed. The same is true for material splashed in the eyes--use an eyewash or a gentle flow of water from a hose. Flushing for at least 15 minutes is recommended. Small splashes on the fingers, hands, or arms usually will not cause any irritation if the material is promptly washed off. These body parts can be easily held in a heavy and continuous flow of water from a sink faucet. Other parts of the body will be more difficult to flush thoroughly and medical attention should be promptly obtained. Obtain medical attention for eye splashes by dialing 911.

Ingestion is unlikely in the laboratory but sudden direct releases or an explosive reaction may cause involuntary swallowing of material sprayed in the face. Neutralizing solutions may be taken if they are immediately available and if prior medical approval has been granted for their use. If these solutions are not available, a large amount of water should be taken at once to afford dilution. Immediately obtain medical attention by dialing 911.

Laboratory spills of bases shall be cleaned using the appropriate spill cleanup kit. The damp mixture can then be scraped up with a plastic, ceramic, or metal scoop. Spill cleanup kits should be kept available throughout the laboratory. Personnel in EMT shall be contacted for disposal of the cleanup materials.

For technical information on specific bases, refer to the MSDS or contact the LaRC IH Contractor or EMT.

#### 7.2 OSHA/IARC/NTP SELECT CARCINOGENS

Carcinogenic materials shall be used only under an approved NASA Langley Form 498. Carcinogenic materials include any material for which OSHA has promulgated an emergency temporary or permanent standard that reflects its carcinogenic potential. A list of materials having this status is in 29 CFR 1910.1450 Appendix B, and thereby are regulated chemicals. Additions to this list may occur. The PHMC may include any other materials it deems appropriate.

OSHA has worked with other agencies on a list of "select carcinogens." These materials are suspect as possible human carcinogens. These suspect carcinogens are defined in 29 CFR 1910.1450(b) and published by the International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP). Additions to the list may occur. It should be noted that materials appearing in OSHA carcinogen standards, on NTP lists, and on IARC lists are on the select list presented. Under the OSHA Hazard Communication standard, materials having OSHA carcinogen standards, or appearing on the NTP Carcinogen Report, or being listed in IARC Group 1 or 2A, shall have reference to their carcinogenic effects in both MSDS's and in material labels.

At LaRC, these "select carcinogens" shall have NASA Langley Form 498's issued to define the procedures for use.

# 7.3 GENERAL LABORATORY SAFETY PROCEDURES

Laboratory fume hoods are in use at several locations at this Center. Basic posting guidelines for safe use of laboratory hoods are in Figure 7.1, Work Practices for Laboratory Hoods. Additionally, a quick posting guide to general laboratory safety is shown in Figure 7.2, Recommended Unit Operations Laboratory Safety Rules.

No large, open-face hood with a low face velocity can provide complete safety for a worker standing at the face against all events that may occur in the hood. The hood may not adequately protect the worker from volatile or otherwise airborne contaminants with a TLV in the low-part-per-billion range. For more ordinary exposures, a properly designed hood in a properly ventilated room can provide adequate protection. However, certain work practices are necessary in order for the hood to perform capably. The following work practices are generally required; more stringent practices may be necessary in some circumstances.

- Conduct all operations that may generate air contaminants at or above the appropriate TLV inside a hood.
- 2. Keep all apparatus at least 6 inches back from the face of the hood. A stripe on the bench surface is a good reminder.
- 3. Do not put your head in the hood when contaminants are being generated.
- Do not use the hood as a waste disposal mechanism except for very small quantities of volatile materials.
- 5. Do not store chemicals or apparatus in the hood. Store hazardous chemicals in an approved safety cabinet.
- 6. Keep the hood sash closed as much as possible.
- 7. Keep the slots in the hood baffle free of obstruction by apparatus or containers.
- S. Minimize foot traffic past the face of the hood.
- Keep laboratory doors closed (exception: some laboratory designs require lab doors to be open).
- Do not remove hood sash or panels except when necessary for apparatus set-up; replace sash or panels before operating.
- 11. Do not place electrical receptacles or other spark sources inside the hood when flammable liquids or gases are present. No permanent electrical receptacles are permitted in the hood.
- 12. Use an appropriate barricade if there is a chance of explosion or eruption.
- 13. Provide adequate maintenance for the hood exhaust system and the facility supply system. Use static pressure gauges on the hood throat, across any filters in the exhaust system, or other appropriate indicators to ensure that exhaust flow is appropriate.
- 14. If the hood sash is supposed to be partially closed for the operation, the hood should be so labeled and the appropriate closure point clearly indicated.

Figure 7.1, Work Practices for Laboratory Hoods.

- 1. "Horseplay" is hazardous and shall not be tolerated.
- 2. Do not work alone in the laboratory at any time except to prepare flow diagrams and operating procedures for equipment.
- 3. Use required personal protective equipment (PPE) whenever specified by the laboratory director.
- 4. Do not wear contact lenses when vapors or fumes are present.
- 5. Wear safety glasses with sideshields and plastic lenses (shall meet ANSI Standard Z87. 1) at all times. Wear splash goggles or face shields as prescribed by the director.
- 6. Do not wear sandals, open shoes, high-heeled shoes, shoes (or boots) with holes in the soles, or shoes with vas uppers; do not wear shorts or skirts. Wear shirts or blouses.
- 7. Secure long hair and loose items of jewelry or clothing when working with rotating machinery.
- 8. Know the use and location of all emergency equipment in the laboratories, shops, and storage areas.
- 9. Know to call 911 to summon emergency response personnel. These 911 number shall be posted at every phone throughout the facility.
- 10. Be familiar with all the elements of fire safety: alarm, evacuation and assembly, fire containment and suppression, rescue, and facilities evaluation.
- 11. Do not use ungrounded wiring and two-wire extension cords. Do not use worn or frayed extension cords or those with broken connections or exposed wiring. Check that electrical devices are grounded before they are turned on.
- 12. Be familiar with an approved emergency shutdown procedure before initiating any experiment.
- 13. Do not deviate from approved equipment operating procedures.
- 14. Keep all laboratory aisles and exits clear and unblocked.
- 15. Do not sniff, breathe, or inhale any gas or vapor unless directed to do so by the laboratory director.
- 16. Label all containers as to content and composition with an appropriate hazard warning. Label the container with the workers name and the date the container was filled.
- 17. Read and obey the instructions on all warning signs.
- 18. Segregate all liquid and solid waste for disposal according to the instructions of the laboratory director. Neutralize all acidic and basic wastes before disposal. Place organic waste material in the designated waste disposal cans; do not pour into any sink or floor drain.
- 19. Practice good housekeeping in the laboratories, shops, and storage areas.
- 20. Do not eat, drink, use tobacco, chew gum, or apply makeup in the laboratories, shops, and storage areas.
- 21. Place only chemicals in the "Chemicals Only" refrigerator and place only food items in a "Food Only" refrigerator. Do not use ice from the ice machine for human consumption or to cool any food or drink
- 22. Report any glassware breakage or malfunctioning instruments or equipment to the teaching assistant.
- 23. Report all injuries, accidents, and "close calls" to the laboratory director. Complete the accident report as soon as possible.
- 24. Report spills of any chemicals to the laboratory director. Follow his/her directions for containment and cleanup. Report all mercury spills to the laboratory director. Follow the prescribed instructions for cleanup and decontamination of all spill areas.
- 25. All personnel shall wash hands their before leaving the laboratories or shops.
- 26. Do not toss tools, supplies, or any other items from one person to another.
- 27. Do not pipette or siphon any material, even water, by mouth.
- 28. Secure compressed gas cylinders at all times. Follow proper safety procedures when moving compressed gas cylinders.
- 29. Use only gauges that are marked "Use no oil" for oxygen cylinders. Do not use an oiled gauge for any oxidizing or reactive gas or any gas that has not been "water pumped."
- 30. Never play with compressed gas hoses or lines, or point their discharges at any person.
- 31. Do not use open flames or heating elements when volatile chemicals are exposed to air.
- 32. Only expose toxic chemicals to the air under a hood. Only expose flammable chemicals to the air under a hood or in an adequately ventilated area.
- 33. Limit personal items brought into the laboratory to those things necessary for the experiment.
- 34. Discourage casual visitors to the laboratory; obtain permission from the laboratory director for visitors to enter. All visitors and invited guests shall adhere to all laboratory safety rules, with adherence being the responsibility of the person visited.

Figure 7.2, Recommended Unit Operations Laboratory Safety Rules.

Chapter 8

#### 8. GENERAL TECHNICAL INFORMATION ON GASES AND CRYOGENS

Most gases including inert gases have some hazards associated with their use. ALL CYLINDERS ARE TO BE CONSIDERED PHM AND TRACKED THROUGH THE CMTS. Any gas stored or used from a compressed gas cylinder has the hazard normally associated with high-pressure vessels or systems, that is, rupture and/or explosive force on release. Some gases have chemical properties, which make them hazardous in other ways, for example, gases which may be flammable, toxic, or explosive when released in a working environment. Other gases (i.e., liquid nitrogen or Helium), though chemically inert, can displace the oxygen of the air and cause asphyxiation of personnel in an area not well ventilated with fresh outside air. Also, any gas, which reacts with  $O_2$ , can cause suffocation under circumstances where  $O_2$  is not replenished. The gases, which are flammable over wide composition ranges with air or oxygen, include hydrogen, carbon monoxide, methane, ethane, acetylene, and propane. The same gases may form explosive mixtures with air or  $O_2$  under certain conditions.

#### 8.1 TOXIC GASES AND CRYOGENS

Toxic gases include carbon monoxide (CO), ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), arsine (AsH<sub>3</sub>), chlorine (CI<sub>2</sub>), fluorine (F<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), and ozone (O<sub>3</sub>). Immediately Dangerous to Life or Health (IDLH) concentrations of gases represent the exposure concentrations at which, in the event of a respirator or ventilation system failure, the exposure is likely to cause death, immediate or delayed permanent adverse health effects, or prevent escape from such an environment.

Some gases normally used in the form of cryogenic liquids or solids have other hazards associated with their use. The low temperatures present local freezing hazards to personnel exposed for a sufficient length of time. Liquid  $H_2$ ,  $O_2$ , and  $F_2$  are very hazardous materials due to the high local concentration of these normally active gases. The powerful oxidizers, liquid  $O_2$  and  $F_2$ , shall be protected from contact with organic materials or fuels as explosive reactions may result. Liquid  $N_2$ , although a relatively inert gas, has its hazards also: (1) the low temperature, (2) (in common with other liquefied gases) if spilled or allowed to evaporate quickly in large quantities in confined areas, can so dilute or replace the  $O_2$  of the air that asphyxiation will ensue, and (3) the liquid  $N_2$  can condense the  $O_2$  from the air making a mixture of liquid  $N_2$  and  $O_2$  which may assume some of the hazards of liquid  $O_2$ , that is, violent reaction with organic compounds.

General safety precautions, for most of the gases covered herein, are to provide good positive ventilation and in the case of the flammable and explosive gases, provide spark and explosion-proof fan motors and electrical equipment. The ventilation system shall be designed with the density of the gas relative to air as a prime consideration. For minor leakage, the gas will follow air streams. For large leaks, separation of gases from air due to density will occur. Normal design for catastrophic failure is for density effects. The American Conference of Governmental Industrial Hygienists (ACGIH) industrial

ventilation manual can be used as a technical reference, or contact the LaRC IH Contractor. Gas bottles being used shall be secured in outside, covered but not enclosed areas, and approved lines used to pipe the gases to the use point. Detection alarm monitors and automatic cut-off valves shall be operating inside the facilities where the hazardous gas is being used. Self-Contained Breathing Apparatus (SCBA) should be available for equipment shutdown where toxic or asphyxiatory situations could develop. The Fire Department shall conduct all rescue operations requiring SCBA. The prime safety precaution shall be to limit concentration of these gases so that the risk of damage is minimized at all times.

For cryogenic liquid gases the precautions shall be to use equipment (e.g. cryogenic gloves, aprons, eye protection) to guard against freezing and avoid spills or very rapid evaporation into an enclosed area. Oxygen deficiency alarm monitors shall be located in areas where spills may occur. SCBA may be required depending on the process and ventilation.

The information furnished here may not provide enough detail for some of the gases listed, particularly H<sub>2</sub> gas and cryogenic liquids. Additional data is available from SFAB, SMAO.

# 8.2 IMMEDIATELY DANGEROUS TO LIFE OR HEALTH (IDLH) CONCENTRATIONS FOR GASES AND SELECTED HAZARDOUS SUBSTANCES

This information can be obtained from the OSHA/National Institute of Occupational Safety and Health Pocket Guide to Chemical Hazards: "Purple Book," June 1990, and "Orange Book", June 1994. The newer version has lower IDLH levels for many of the substances. In May 1996, however, OSHA decided that the rationale for the June 1990 IDLH guidelines shall be followed. Both are listed herein for information purposes.

The 1990 IDLH's shall be used at LaRC. As a guide, processes involving gases with IDLH's of 5,000 ppm or less shall have NASA Langley Form 498. For example, operations involving 0.5 percent (5,000 ppm) methyl bromide (IDLH of 2000 ppm) shall require a NASA Langley Form 498. Others above 5,000 may require a NASA Langley Form 498 depending on the volume and use conditions.

For additional information on these substances, contact SFAB, SMAO.

#### 8.3 GAS AND LIQUEFIED HYDROGEN

This paragraph is designed to cover most aspects of hydrogen handling and usage pertaining to personnel and equipment. It is the intent to present acceptable hydrogen standards and practices for minimum safety requirements only. More extensive safety precautions shall be employed when there is extra hazard, as in highly congested areas or in operations with equipment that has little safety margin.

# **8.3.1 Safety**

Hydrogen operations shall be carried out in such a way that the life and health of personnel are not jeopardized and the risk of damage to property is minimized.

The following principles shall be adopted:

- Inherent safety Hydrogen systems and operations shall have a high degree of built-in safety. Safety shall be attained by design, construction, and procedures while observing all three of the basic axioms for hydrogen safety: adequate ventilation, leak prevention, and elimination of ignition sources.
- Two lines of defense In addition to the inherent safety features, at least two
  barriers or safeguards shall be provided to prevent a given failure from
  mushrooming into a disaster. For instance: one safeguard against spillage might
  be a leak detector, which automatically shuts off the flow; a second might be a
  shield to protect other equipment and a safe shelter for personnel.
- Proper controls Safety functions such as leak detection and ventilation shall be automatically controlled. Operating functions such as flow rate and pressure may be controlled either automatically or manually, as appropriate to the system. However, even simple tests shall require automatic control if prolonged or repetitive, because of the tendency for personnel to become inattentive and careless. In any case, manual controls shall be constrained by automatic limiting devices to prevent over-ranging.
- Fail-safe design Whenever possible, failure (including momentary failure) of equipment, power, or other service shall cause the system to revert to the condition which will be safest for personnel and property.
- Alertness Employees shall be ever alert to all aspects of safety. They shall
  constantly reexamine procedures and equipment to be sure safety has not been
  compromised or impaired by changes in program or test methods, overfamiliarity
  with the work, deterioration, or stresses due to abnormal conditions, and so forth.
- NFPA 50A and NFPA 50B contain information (i.e. grounding, bonding, and electrical) on installation of gaseous and liquid mobile hydrogen supply systems, respectively.

#### 8.3.2 Nature of the Hazard

The nature of the hazard from hydrogen is identified by its properties (gaseous and liquid), explosion/detonation potential, and diffusion or leakage.

# 8.3.2.1 Properties and Hazards of Gaseous Hydrogen

Gaseous hydrogen has the following properties:

Specific gravity, 68° F (air = 1.00)	0.06953
Density, lb/ft <sup>3</sup> (60° F and 30" of Hg)	0.00532
Density, lb/ft <sup>3</sup> (-422.9° F and 30" of Hg)	0.084
Specific volume, ft <sup>3</sup> /lb (60° F and 30" of Hg)	187.9
Critical temperature, <sup>o</sup> F	-399.80
Gross heat of combustion, Btu/ft <sup>3</sup>	325.1
Gross heat of combustion, Btu/lb	61.084
Btu/ft³ of stoichiometric gas/air mixture (F/A ratio, 0.418 vol., 0.029 wt.; or 29.5% H₂ by vol.)	81.3
Ft <sup>3</sup> of air required per ft <sup>3</sup> of combustible	2.382
Lb air required per lb combustible	34.226
Maximum flame temperature, $^{\rm 0}$ F (F/A ratio, 0.462 vol., 0.0313 wt.; or 31.6% H $_{\rm 2}$ by vol.	3865
Autoignition temperature in air, ° F (14.7 psia)	854 - 1070
Autoignition temperature in oxygen, <sup>o</sup> F (14.7 psia)	859 - 1039
Flammability limits, % vol. H <sub>2</sub> in air	4.0 - 75.0
Flammability limits, % vol. H <sub>2</sub> in oxygen	4.5 - 94.0
Detonation limits, % vol. H <sub>2</sub> in air	18.3 - 59.0
Detonation limits, % vol. H <sub>2</sub> in oxygen	15.0 - 90.0
Nonflammable limits, air-hydrogen-carbon dioxide	less than 8% O <sub>2</sub>
Nonflammable limits, air-hydrogen-nitrogen	less than 5% O <sub>2</sub>
Minimum spark ignition energy in air, J (atmospheric pressure)	0.000019
nimum spark ignition energy in oxygen, J (atmospheric pressure)	0.000007

# 8.3.2.2 Hazards of Gaseous Hydrogen

The following hazards exist for gaseous hydrogen:

- Hydrogen gas is colorless and odorless, thus it is not detectable by the senses.
- Although not toxic, hydrogen gas can cause suffocation by diluting air to exclude oxygen.
- At normal temperatures, hydrogen gas is lighter than air so that it tends to rise.
   But, if the temperature of hydrogen gas is less than -418° F, as just after

evaporation from the liquid, it is heavier than air at normal temperatures and tends to fall; however, wind or forced ventilation will affect the direction of motion of released hydrogen regardless of its rising or falling tendency.

- When mixed with air or oxygen, hydrogen gas forms a highly flammable mixture over a wide range of mixture ratios (above).
- Ignition of explosive mixtures occurs with very low energy input, one-tenth that of a gasoline-air mixture. An invisible spark can cause an explosion.
- Temperatures of about 1000° F are usually required for the autoignition of hydrogen and air or oxygen mixtures presented above. However, at less than atmospheric pressure, that is, at 0.2 to 0.5 atmosphere autoignition will occur if temperatures as low as about 650° F are maintained long enough.
- Hydrogen burns with a pale blue almost invisible flame. Visibility is caused by impurities.
- Severe burns have been suffered by persons exposed to hydrogen flames resulting from the ignition of hydrogen gas escaping from small leaks in laboratory apparatus.

# 8.3.2.3 Properties of Liquid Hydrogen

The following is a list of the properties of liquid hydrogen:

Melting point at atmospheric pressure, ° F		-434.6° F
Boiling point at atmospheric pressure, <sup>o</sup> F		-423.2° F
Critical temperature, <sup>o</sup> F		-399.8° F
Critical pressure, atm		12.8 atm
Specific gravity (liquid, water = 1.00)		0.07 (4.37 lb/cu ft)
Specific heat, Btu/lb/o F		0.57
Heat of fusion, Btu/lb		25.2
Viscosity, poises (at normal boiling point)		132 X 10 <sup>-6</sup> poises
Heat of vaporization, Btu/lb (nearly all para)		190.5 Btu/lb
Vapor pressure, psig at:	-433° F	-12.8
	-423° F	0
	-420 ° F	9.0
	-402° F	147.3

# 8.3.2.4 Hazards of Liquid Hydrogen

The following hazards exist for liquid hydrogen:

- All of the hazards, which exist when gaseous hydrogen is present, are equally serious with liquid hydrogen because of the ease with which the liquid evaporates.
- People have died from exposure to rather small local flash fires resulting from the ignition of gas produced by the evaporation of small amounts of liquid hydrogen.
- The continuous evaporation of liquid hydrogen in a dewar causes the constant generation of gaseous hydrogen, which must be either vented to a safe location or temporarily confined in a safe manner.

 Vents from storage dewars containing liquid hydrogen may be closed by accumulations of ice frozen from moisture in the air. Excessive pressure may then rupture the container and release a quantity of hydrogen.

- Liquid hydrogen is subject to contamination with air condensed and solidified from the atmosphere or by accumulation of traces introduced in manufacturing. This mixture is unstable and may detonate with effects similar to those produced by TNT and other high explosives.
- Liquid hydrogen splashed on the skin or in the eyes can cause serious freezing "burns".

# 8.3.2.5 Explosion and Detonation of Hydrogen-Air Mixture

Hydrogen gas, like other fuels, can burn in two modes. The ordinary mode of burning is called deflagration, in which the flame travels through the mixture at subsonic speeds. This happens, for instance, when an unconfined cloud of hydrogen-air mixture is ignited by a small ignition source. Under these circumstances, the flame will travel anywhere from ten to several hundred feet per second. The rapid expansion of hot gases produces a pressure wave. Witnesses will hear a noise, often a very loud noise, and may say that an explosion occurred. The pressure wave from rapid unconfined burning is not extremely severe, although it may well be strong enough to damage nearby structures. The other mode of burning is called detonation, in which a flame and shock wave travel together through the mixture at supersonic speed. A detonation will often build up from an ordinary deflagration that has been ignited in a confined or partly confined mixture. This is true even though ignition may have been caused by a minimal energy source. On the other hand, it takes a powerful ignition source to produce detonation in an unconfined hydrogen-air mixture (for example, a blasting cap, a few grams of high explosive, or an exploding wire). The pressure ratio across a detonation wave in a hydrogen-air mixture, as seen when the wave passes a detector mounted flush in a confining wall, is about 20. (A pressure ratio of 20 means 300 psia if the mixture is at atmospheric pressure.) When the wave strikes an obstacle, the pressure ratio seen by the obstacle is multiplied two to three times, or 40 to 60. Even larger pressure ratios occur locally in the region when a deflagration transforms to a detonation.

# 8.3.2.6 Diffusion and Leakage of Hydrogen

Hydrogen may diffuse or leak as follows:

#### Diffusion

- Hydrogen diffuses approximately 3.8 times faster than air. A spill on the ground of 500 gallons of liquid hydrogen will have diffused to a nonexplosive mixture after about 1 minute.
- Air turbulence increases the rate of hydrogen diffusion.

#### Leakage

 Hydrogen in both the liquid and gaseous states is particularly subject to leakage because of its low viscosity and low molecular weight. Leakage is inversely proportional to viscosity. Because of its low viscosity alone, the

leakage of liquid hydrogen will be roughly 100 times that with JP-4 fuel, 50 times that with water, and 10 times that with liquid nitrogen. Likewise, the leakage of gaseous hydrogen will be approximately twice that for air.

# 8.3.3 Operating Instructions

For installations, which require any operation of equipment by the user, legible instructions shall be maintained at operating locations. A qualified person shall be in attendance at all times while the mobile hydrogen supply unit is being unloaded. Each mobile liquefied hydrogen supply unit used as part of a hydrogen system shall be adequately secured to prevent movement. The mobile liquefied hydrogen supply unit shall be grounded for static electricity in accordance with the Standard on Static Electricity, NFPA 77.

# 8.3.4 Siting of Bulk Storage Areas

General and specific requirements for siting of bulk storage areas are presented herein. Gaseous hydrogen systems are required to be located in accordance with NFPA 50A, Chapter 3. Coordinate with the LaRC Fire Chief for specific siting requirements.

#### 8.4 LIQUID NITROGEN

This data is designed to cover most aspects of liquid nitrogen handling and usage. Both personnel and equipment are concerned. It is the intent to present here acceptable liquid nitrogen standards and practices for minimum safety requirements only. More extensive safety precautions shall be employed when there is extra hazard, as in highly congested areas or in operations with equipment that has little safety margin.

### 8.4.1 Physical Properties of Nitrogen

The following is a list of the properties of liquid nitrogen:

Boiling Point -320.5° F Freezing Point -346° F

Liquid Density 50.48 lb/ft<sup>3</sup> at -320.5° F

Critical Pressure 493 psia Critical Temperature -232.5° F

#### 8.4.2 Personnel Education

The following items concerning liquid nitrogen shall be thoroughly explained to all persons working with its storage, handling, or transfer:

- The principal hazard of liquid nitrogen is its extremely low temperature.
- The nature and properties of nitrogen in both the liquid and the gaseous states must be emphasized due to the extremely low temperature of liquid nitrogen and its ability to exert excessively high pressures in closed systems, if allowed to

warm from normal storage temperatures to temperatures near the critical temperature (-232° F).

- An oxygen deficiency hazard can result from the vaporization of liquid nitrogen.
- Compatible construction materials shall be used.
- Proper equipment, operated properly, shall be used.
- Use and care of appropriate personal protective equipment and clothing.
- Safety measures, self-aid, and first aid (by dialing 911).
- Trained supervision shall be provided for all potentially hazardous activities involving liquid nitrogen.
- All operations involved in handling more than laboratory amounts of liquid nitrogen shall be performed by persons working in groups of two or more. The information presented in Figure 8.1, "Liquid Nitrogen," shall be posted at any operational site where liquid nitrogen is involved.

#### 8.4.3 Personal Protection

Personal protection includes hand, foot, head, face, body, and respiratory protection.

#### 8.4.3.1 Hand and Foot Protection

Hand protection shall be worn because contact with liquid nitrogen or an uninsulated liquid nitrogen container may result in injury. Cryogenics gloves are preferable; however, leather gloves can be safely used in an emergency and for short periods of time. The gloves shall be loose fitting for easy removal in the event liquid nitrogen runs into the glove.

High-top leather footwear shall be worn to keep liquid nitrogen from getting inside. Trouser legs shall be cuffless and worn outside the shoe tops.

# 8.4.3.2 Head, Face, and Body Protection

Head and face protection (acid-type goggles or a face shield, which will stop splashes coming from any direction, such as a nitro-meter mask or hood) shall be worn by those handling liquid nitrogen.

# LIQUID NITROGEN (To be posted at operations site)

# **Hazards**

- 1. Skin contact causes frostbite and "burns."
- 2. Liquid nitrogen is nontoxic and does not produce irritating fumes. Skin or eye contact with liquid nitrogen, however, will result in freezing of the tissues. The injury is similar to that of a burn, and the effect is usually called a burn.
- 3. Nitrogen gas is odorless, nonflammable, inert and nontoxic; however, it may replace oxygen in the atmosphere and thus cause asphyxiation. Under no condition should personnel enter a tank or a closed space until normal oxygen concentration has been reestablished and until all connections to the tank have been blanked or positively closed off. The atmosphere must be checked frequently and an observer stationed outside to check the operator's reactions.

# First Aid

If liquid nitrogen is spilled on the skin, the preferred action is immersion of the affected area in nonflowing, tepid (100 - 112° F) water. Use of high-pressure showers or jets is not the primary emergency action due to the inability to control temperature and/or flow rate. If a person loses consciousness, immediately remove them to an open space, dial 911 for medical attention, and apply artificial respiration.

#### **Safety Precautions**

- 1. All personnel shall be familiar with the nature and characteristics of liquid nitrogen.
- 2. Persons engaged in operations involving handling or transfer of liquid nitrogen shall wear the approved goggles or face shields, protective clothing, gloves, and shoes.
- 3. Operations involving the handling of liquid nitrogen shall be performed by two or more persons working in groups.
- 4. Care shall be taken to prevent accumulation of moisture in lines, valves, traps, and so forth, to avoid freezing, plugging, and subsequent possibility of pressure ruptures. Care shall also be taken to prevent entrapment of liquid nitrogen in unvented sections of the system.
- 5. Immersion tanks or safety showers shall be inspected periodically and prior to any operation involving liquid nitrogen, and if outside, shall be protected from freezing.
- 6. The storage, use, and disposal of liquid nitrogen shall be in well-ventilated areas.
- 7. Liquid nitrogen that is to be used should not be exposed to the air for any length of time.

Figure 8.1, Liquid Nitrogen.

An approved apron shall be worn if liquid nitrogen is being handled in an open system. If liquid nitrogen is spilled onto clothing of absorbent material such as wool, it will be absorbed and retained in contact with the body causing burns. Therefore, a limited-protection suit of nonabsorbent material is recommended where gross spillage or splashing is possible.

# 8.4.3.3 Respiratory Protection

Respiratory protection of the self-contained type shall be required in unventilated areas where liquid or gaseous nitrogen is handled, except where small quantities are involved. Canister-type masks are ineffective and shall not be used for protection against nitrogen asphyxiation.

# 8.4.4 Toxicity

No health hazards result from breathing nitrogen gas provided sufficient oxygen is present in the atmosphere. The main hazard from liquid nitrogen arises from its very low temperature. Serious burns and frostbite can occur when liquid nitrogen comes in contact with body surfaces. Burns from liquid nitrogen should be kept clean; and immediate medical treatment sought. The immediate effects of frostbite may be lessened by

soaking affected parts in tepid water (100 -112° F). After accomplishing immediate selfaid, dial 911 for medical assistance.

#### 8.4.5 Fire Hazards

Liquid nitrogen, if uncontaminated, presents no fire hazard. Care shall be observed to avoid contamination with combustible materials or oxidizers, especially oxygen, if the nitrogen is to be used for pressurizing propellant systems. In emergency situations liquid nitrogen may be used as a fire-extinguishing agent since it acts to occlude air or oxygen by forming a weak gas blanket.

# 8.4.6 Explosion

Pure liquid nitrogen presents no explosion hazard. However, if confined without adequate vent or relief systems, liquid nitrogen can absorb heat energy and generate internal pressure leading to explosion and rupture of the container. Undetected contamination with combustibles or oxygen could result in a serious explosion if contaminated nitrogen is introduced into a closed system containing substances with which these contaminants react. In transfer operations, liquid nitrogen should not be exposed to air; otherwise, oxygen from the atmosphere will condense in the liquid nitrogen.

Pressure rupture may occur when liquid nitrogen is trapped in a closed system and refrigeration is not maintained. Nitrogen cannot be maintained as a liquid if its temperature rises above -232.5° F regardless of confining pressure. Liquid nitrogen trapped between valves can cause violent rupture of the pipe or tube. Loss of

refrigeration can cause the storage tank to rupture if the nitrogen is not dumped or pressure relieved by suitable devices. Loss of vacuum in vacuum-jacketed tanks can cause increased evaporation and overload the normal venting system, resulting in high pressures.

#### Preventive actions include:

- All sources of contamination shall be eliminated from nitrogen transferring and servicing operations.
- Pressure rupture of equipment can be avoided by checking all parts of the
  nitrogen system to see that refrigeration and/or vacuum-jacketing is maintained.
  Closed systems and "dead ends" shall be avoided unless properly protected with
  pressure relief valves and blowout discs. LPR 1710.40, "Safety Regulations
  Covering Pressurized Systems," in the LaRC Facility Systems Assurance
  Manual, contains system design requirements.
- To prevent asphyxiation, adequate precautions shall be taken in areas where high gaseous generation from liquid nitrogen may occur. Ventilation and/or selfcontained breathing apparatus may be required.
- Protective equipment and clothing shall be worn when accomplishing operations on an open system or when performing maintenance on a defective, leaking system.

## 8.4.7 Transfer and Storage

In the handling of liquid nitrogen, two important factors shall be taken into account: liquid nitrogen is extremely cold, having a boiling point of about -320° F, and, if evaporated, it is an asphyxiant. Liquid nitrogen shall, therefore, be stored in containers either fixed or mobile, of approved design, materials, and construction, and suitably housed.

Storage, transfer, and test areas shall be kept neat and free from combustibles. These areas shall be frequently inspected.

Approved type immersion tanks or safety showers shall be located for immediate use. In moving large containers of liquid nitrogen, trucks or dollies shall be used to minimize the possibility of spillage. In general, the precautions taken in handling liquid nitrogen are very similar to those for liquid oxygen. Self-aid immersion tanks or safety showers shall only be located in proximity to high operational frequency bulk storage filling stations where smaller portable dewars are filled or other open transfer operations are common.

### 8.5 LIQUID OXYGEN

High purity liquid oxygen is a light blue transparent liquid. It boils vigorously at ambient conditions and uninsulated containers usually become frosted. Oxygen has no odor.

### 8.5.1 Chemical Nature

In either gaseous or liquid form, oxygen is a strong oxidizer, which vigorously supports combustion. The violence of some reactions involving liquid oxygen is due to the enrichment of the air in the vicinity of evaporating liquid to a higher-than-normal concentration of oxygen.

Liquid oxygen is completely mixable with nitrogen, fluorine, and methane. Light hydrocarbons are usually soluble in liquid oxygen; acetylene is soluble only to about 4 parts per million.

Pure liquid oxygen is chemically stable. It is not shock sensitive and will not decompose. At ordinary temperatures in properly designed containers, the 24-hour evaporation rate may be as low as 1.4 percent from a 450-gallon container and 0.4 percent from a 1,350-gallon container.

# 8.5.2 Physical Properties

The major physical properties of oxygen are listed in the following:

Boiling Point	-297.4° F
Freezing Point	-361.3° F
Liquid Density71.23 lb/ft <sup>3</sup> at	-297.4° F
Critical Pressure	731.4 psia
Critical Temperature	-181.4° F

#### 8.5.3 Hazards

The principal hazards associated with the handling of liquid oxygen are as follows:

- Exposure of the body to the liquid or cold vapors.
- Fire supported by the liquid oxygen.
- Shock detonation of liquid oxygen in contact with combustible material.

#### 8.5.4 Health Hazards

The health hazards of liquid oxygen are associated with its very low temperature. The low temperature of liquid oxygen may cause frostbite when the liquid, or uninsulated piping containing it, contacts the skin. Breathing pure oxygen for limited periods of time (an hour or two) will not cause any toxic effects, however, the upper respiratory tract may become irritated if the gas is very cold.

### 8.5.5 Fire and Explosion

Fire and explosion hazards include ignition, fire, and explosion as follows:

Oxygen is not hypergolic with fuels, that is, spontaneous ignition does not occur
when liquid or gaseous oxygen contacts a combustible material. However,
ignition can occur very readily. For example, liquid oxygen and liquid fuels, when
brought together, form slurries or mixtures that are shock-sensitive. The same is
true of many solids, such as asphalt or wood that have a porous structure and
can become saturated with oxygen. In the oxygen-enriched atmosphere that
surrounds evaporating liquid, ignition is more likely and occurs with much weaker
sparks and lower temperatures than would be the case in air.

- Oxygen supports vigorous or even violent burning. Materials that burn only sluggishly or not at all in the air burn quickly in oxygen. Almost any material will burn. For example, Teflon and silicones, which are generally regarded as fireproof or fire resistant, can burn easily in oxygen under the right conditions. Such common fuels as kerosene, cloth, wood, and paint burn violently. Even metals are not immune. Titanium can detonate when in contact with liquid oxygen and most other metals will burn once ignited. Gaseous fuels ignite more readily and burn faster with oxygen vapor or oxygen-enriched air than with normal air. There is a greater chance that such burning will progress to the detonation stage. Moreover, the limits of flammability, particularly the upper (rich) limit, is widened, which means that fire and/or detonation is possible over a greater range of mixtures.
- It has already been mentioned that slurries or mixtures of liquid oxygen and liquid fuels are shock-sensitive. This means that they can be ignited by a blow, by dripping, or by water-hammer effect. Such mixtures can also be ignited by flames or hot surfaces, and by sparks, including the electrostatic discharges that are automatically generated in the process of mixing the liquid oxygen and the fuel. Once ignited, a detonation occurs with effects like those of TNT or other high explosives.

### 8.5.6 Pressure Rupture

Oxygen cannot be kept liquid if its temperature rises above the critical temperature of 181.4° C. Consequently, if liquid oxygen is trapped in a closed system and allowed to warm up, extreme pressures can build up and rupture the system. For example, liquid oxygen trapped between valves can rupture the connecting pipe. Closed systems and "dead ends" shall be avoided unless properly protected with pressure relief valves and blowout discs. Moreover, relief and vent systems shall be sized to accommodate the flow so that excessive back pressures will not be imposed on the equipment the relief system is supposed to protect. Sizing is especially important in the case of vacuum-jacketed tanks, where loss of vacuum will cause very rapid vaporization of the liquid.

### 8.5.7 Safety Measures

All operations involving the handling of liquid oxygen shall be performed using a "Buddy System" approved by the LaRC Safety Manager.

### 8.5.7.1 Training of Personnel

The following subjects shall be thoroughly explained to all persons concerned with the handling, transfer, and storage of liquid oxygen:

- Nature and properties of oxygen in both the liquid and gaseous phases.
- Approved materials that are compatible with liquid oxygen.
- Proper equipment and its operation.
- Use and care of protective equipment, clothing, and safety equipment.
- Self-aid and medical attention.
- Necessity of maintaining a clean system and clean equipment in oxygen service.

### 8.5.7.2 Safety Clothing

Safety clothing, as follows, shall be required for personal protection:

- Hand and foot protection For work around cryogenic systems, gloves shall have good insulating quality. They shall be designed for quick removal in case liquid oxygen gets inside. Shoes should have high tops and pants legs should be worn outside and over the shoe tops. The shoes should be leather.
- Head, face, and body protection Personnel handling liquid oxygen shall wear a
  face shield or hood with face shield. If liquid oxygen is being handled in an open
  system, an apron of impermeable material should be worn.

Oxygen will saturate normal clothing, rendering it extremely flammable. Clothing described as flame-resistant or flame-retardant under normal atmospheric oxygen concentration cannot be relied upon to provide adequate flame protection in an oxygen-enriched atmosphere. Clothing components, which have good insulative properties and are impermeable, may be effective under cryogenic spill conditions.

### 8.5.7.3 Other Safety Equipment

Portable oxygen detectors of approved design are useful in situations where oxygen leakage may increase fire and explosion hazards. Safety showers and eyewash functions shall not be used to treat cryogenic burns (frostbite) as they will do more harm than good. Showers and eyewash functions are provided only to deal with fire and corrosive chemicals.

### 8.5.7.4 Smoking Regulations

Smoking and open flames are prohibited within a minimum of 50 feet of a liquid oxygen system.

### 8.5.7.5 Drainage and Diking

All storage facilities containing liquid oxygen shall be drained or diked to prevent damage in other areas if a tank should rupture or a dump should be necessary. Spilled or dumped oxygen shall be prevented from mixing with incompatible propellants or materials, and shall not block established routes of personnel exit. If diking is used, the

dike shall be concrete and high enough to contain 110 percent of the capacity of the storage vessels.

### 8.5.7.6 Electrical Equipment

Electrical equipment containing sparking devices or hot surfaces shall be excluded from storage areas or transfer facilities. Oil bath exclusion devices shall not be used.

#### 8.5.7.7 Access Roads

At least two access roads to transfer and storage sites shall be provided, each wide enough to give adequate space for turning trucks.

### 8.5.7.8 Safety Equipment

An adequate water supply shall be provided for flushing and decontamination. For high frequency operational areas (e.g, filling dewars, transfer operations), immersion water tanks having controlled temperature shall be considered for location in close proximity to the affected area. There should be facilities near the storage area for safety clothing and equipment. The condition of safety clothing and equipment shall be checked frequently by first-line supervision.

#### 8.5.7.9 Ventilation

Areas in which liquid oxygen is handled shall always be well ventilated to prevent excessive concentration of gas. Never dispose of the liquid in confined areas or in places that others may enter.

# 8.5.7.10 Housekeeping

Areas surrounding storage sites shall be kept free of grease, oil, oily waste, and all other organic materials, including vegetation. Smoking, sparks, and open flames are not permitted in storage areas. Frequent inspections shall be made to ensure good housekeeping.

#### 8.5.7.11 Siting Requirements for Storage of Liquid and Gaseous Oxygen

Siting requirements for storage of liquid and gaseous oxygen shall be in accordance with requirements of OSHA regulation 29 CFR 1910.104 and the LaRC Fire Chief.

# 8.5.8 Systems and Equipment Cleaning

Since many special problems and circumstances are encountered when systems are prepared for use with oxygen, no single cleaning procedure can be specified that will meet all field requirements. For specific instructions varying with materials of construction, see LPR 1740.5, "Procedures for Cleaning of Systems and Equipment for Oxygen Service."

### 8.5.9 Transfer Operations

Storage, transfer, and test areas shall be kept neat and free from combustibles and shall be inspected frequently. An adequate water supply shall be available for

firefighting. The operation of transfer equipment shall be determined by local designs and construction, the type of equipment selected, and the procedures prescribed by either the cognizant authority or the equipment manufacturer. All personnel shall be completely and thoroughly instructed before operating the equipment. All valves, pumps, and switches shall be identified and tagged.

Check-off sheets and written instructions are substantial aids to safe operations and shall be required for all but the simplest installations. In addition to checklist items pertaining to the specific equipment, there shall also be a list of general safety measures that may be required, such as ventilation, posting and barricading, notification of safety forces, and so forth.

After extended use and after periods of extended shutdown, inspections shall be made for possible contamination and for evidence of unsafe equipment conditions.

The filling rate shall be such as to minimize thermal shock in the receiving vessel and lines.

# 8.5.10 Transportation

This section covers applicable laws and marking for transportation. Practically all liquid oxygen is shipped at atmospheric pressure or at gage pressure of only a few psi. Since the Department of Transportation (DOT) definition for compressed gas excludes any commodity carried at a pressure of less than 40 psia, these shipments are not classed or regulated by the DOT as a compressed gas.

### **8.5.10.1 Packaging**

Shipping containers are generally vacuum-insulated tank cars, tank trucks, and portable tanks. All shall be fitted with relief valves that discharge to the atmosphere. Liquid oxygen tanks exceeding 150 gallons that are shipped in closed boxcars or trucks shall have discharge vents or relief valves venting to the outside atmosphere. Shipping tanks and their insulation should be made of noncombustible materials. If the insulation is contained by an outer metal jacket, the jacket shall have a pressure-relief device, so in case of a leak, pressure will not build up and rupture the vessel.

- DOT Land transportation Specification DOT-4L describes cylinders for transportation use, which are limited to a maximum capacity of 1000 pounds of water and pressures of 40 to 500 psig. Liquid oxygen may be shipped in such a container. It is by DOT definition a nonflammable compressed gas and is termed "pressurized liquid oxygen." Tank cars and tank trucks carrying liquid oxygen at less than 25 psig are not affected by this regulation.
- Federal Aviation Administration (FAA) Commercial air specifications, "Official Air Transport of Restricted Articles Tariff-6D" (ref. 8), authorize 150 pounds maximum quantity of liquid oxygen aboard passenger aircraft and 300 pounds maximum quantity oxygen aboard a cargo aircraft when carried in DOT-4L specification containers.

 Department of Defense (DOD) - Military air specifications, Air Force Manual (AFM) 71-4, "Packaging and Handling of Dangerous Materials for Transportation by Military Aircraft" (ref. 9), list unpressurized liquid oxygen as acceptable, but no more than six dewars of 25-liter capacity can be carried aboard an aircraft.

 United States Coast Guard (USCG) - Waterways specifications-Refer to DOT Regulations and Coast Guard Regulation CF-108 (ref. 10) for packaging and handling information.

### 8.5.10.2 Marking

Liquid oxygen at pressures over 25 psig is defined by DOT as nonflammable compressed gas and a green label is required on such regulated shipments.

### 8.5.10.3 Transportation Accident Procedure

If there is a spill or leak, shut off the ignition. Do not smoke or light flares. Evacuate the area and keep the public upwind. Do not walk or roll equipment over the spill area until all frost is gone. Use gloves and goggles or a face shield to enter the spill area. Shut off the leak if it can be done without risk. Fog (condensed moisture) usually indicates the vapor area.

- In case of fire, use water to cool tanks exposed to the fire. If a substantial part of the insulation jacket and the insulation are lost, vacate the area, as the tank may rupture.
- If operators have been exposed to liquid oxygen vapor, clothing will be saturated with oxygen and will be dangerously flammable. Air clothing thoroughly; it may remain in a hazardous condition from 10 minutes to over an hour, depending on the kind of cloth and tightness of weave. Do not smoke or approach ignition sources with oxygen-impregnated clothing. Body hair also tends to become saturated and will trap oxygen close to the skin. Showering eliminates this hazardous condition.
- If operators have been contacted by liquid oxygen or cold hardware and have suffered "cryogenic burns," the preferred action is immersion of the affected part in tepid water (100°-112° F). Use of high-pressure showers or jets of water on frozen flesh should be avoided. As soon as immediate on-the-scene action has been taken, prompt medical attention should be obtained for the affected party.
- Report details of the accident in accordance with LMS-CP-4760, "Reporting Injuries, Illnesses, Compensation Claims and Unsafe Working Conditions." and Potential Violations of Occupational Safety/Health Standards."

# 8.5.11 Emergency Procedures

The primary danger from a spill or a leak is a fire or explosion from combustible materials in the presence of a high concentration of oxygen gas. Ventilation will minimize the danger around indoor equipment.

### 8.5.11.1 Firefighting

Procedures for controlling fires involving liquid oxygen vary with the type and circumstances of the fire. The following general recommendations shall be used as a guide. When the fire results from a leak or flow of liquid oxygen onto wood, paper, waste, or other similar material, first stop the flow if possible. If the leak or flow can be stopped, use water to put the fire out quickly. When the fire involves liquid oxygen and liquid fuels, control it as follows:

- Dial 911.
- If the fuel and liquid oxygen are mixed, but not burning, isolate the area from sources of ignition, quickly evacuate personnel, and allow the oxygen to evaporate. Mixture of fuel and liquid oxygen present an extreme explosion hazard.
- If a fire is supported by liquid oxygen flowing into large quantities of fuel, shut off the flow of oxygen. After that has been done, put out the fire with water fog, foam, or "light water."
- If a fire is supported by fuel flowing into large quantities of liquid oxygen, shut off
  the flow of fuel and allow the fire to burn out. If other combustible material in the
  area is burning, water streams or fogs may be used to control the fires. DO NOT
  apply foams to liquid oxygen.
- If large pools of oxygen and water-soluble fuels such as hydrazine or alcohol are burning, use water to dilute the fuel and reduce the intensity of the fire.

#### 8.5.11.2 First Aid and Self-Aid

Parts of the body that have been frozen by contact with liquid oxygen should be treated by soaking in tepid water (100° - 112° F). As soon as immediate on-the-scene action has been taken, prompt medical attention shall be obtained for the affected party by dialing 911 for medical assistance.

### 8.5.12 Disposal

Uncontaminated liquid oxygen is best disposed of by allowing the liquid to vaporize from normal heat leak into the container and the vapor to escape through the vent. Liquid oxygen may also be piped into an area free from combustible material and allowed to vaporize.

When liquid oxygen has been contaminated by fuel, isolate the area from sources of ignition and quickly evacuate personnel. Allow the oxygen to evaporate and the residual fuel gel to reach ambient temperatures. Inert the oxygen system with gaseous nitrogen prior to any other cleanup step.

#### 8.6 SILANE

Silane at room temperature and atmospheric pressure is a colorless gas with a repulsive musty odor. It is stable indefinitely in metal containers. Silane in the pure state is spontaneously flammable (pyrophoric) in air. It is shipped in various size steel

cylinders as a nonliquified gas at various pressures, the highest cylinder pressure being 8625 kPa (1250 psig) at 21.1° C.

### 8.6.1 Chemical Properties

Silane is readily oxidized by air and forms spontaneously flammable or explosive mixtures. At certain flow rates and concentrations, explosions may occur after several seconds time delay. Silane is attacked by water in the presence of even minute traces of hydroxyl ion to evolve hydrogen and form hydrated silica or silicic acid. Silane is stable to acid water. Silane is a strong reducing agent. Halogenation reactions with chlorine or bromine are explosively violent at room temperature. Decomposition of silane into silicon and hydrogen begins at about 400° C and proceeds rapidly at temperatures above 600° C.

### 8.6.2 Physical Properties

The physical properties of silane include:

Molecular Weight 32.112 Specific Volume @ 70° F, 1 atm 12.0 cu. ft./lb (749.1 ml./g.). - 168.50 F (- 111.4) Boiling Point @ 1 atm Freezing Point @ I atm -303.5° F (-186.4° C) Density, Gas @ 0° C, 1 atm 1.44 g./l. Density, Liquid @ -185° C 0.68 g./ml. Critical Temperature 25.70° F (-3.5° C) 702.7 psia (47.8 atm), (49.3 kg./cm.<sup>2</sup> absolute) **Critical Pressure** 10.24 cal./(mole), [0.319 cal./(g.) (C°)] Heat Capacity, Gas @ 250 C, 1 atm, Cp Viscosity, Gas @ 15° C, 1 atm 112.4 micropoises 48.79 cal. (mole) (C°), [1.52 cal/(g.) (C°)] Entropy, Gas @ 25° C, 1 atm Heat of Formation, Gas @ 25° C  $7.2 \pm 0.3$  kcal./mole (227.3 ± 9.3 cal./g.)

### 8.6.3 Toxicity

Little is known of the toxicity of silane except that breathing this gas in low concentrations, probably less than one molar percent without spontaneous ignition, may cause headache and nausea. The hydrolysis of silane in the body tissues would form silicic acid or hydrated silica. The offensive odor should be taken as a warning of the presence of dangerous concentrations.

Silane has low acute toxicity by inhalation in laboratory animals, the four-hour mouse  $LC_{50}$  being 9600 ppm and that for the rat, 4000 ppm; on the rabbit skin, the  $LD_{50}$  is 3540 mg/kg.

A TLV for personnel exposures of 5.0 ppm (approximately 6.6 mg/m³) was adopted by the American Conference of Governmental Industrial Hygienists (ACGIH) on the basis of its acute toxicity in laboratory animals relative to other hydrides of metalloids.

# 8.6.4 Safety Measures

General precautions for handling and storage of compressed gas cylinders shall be taken. In addition, the following specific precautions shall be observed in handling silane:

- Installation of all silane piping and equipment shall always be in a well-ventilated area. Avoid installations, which could cause vented or leaking silane to accumulate, such as inside a gas cabinet, enclosure, trench, or room. Accumulation of vented or leaking silane may create a severe explosion hazard.
- Piping and equipment should be thoroughly pressure-checked with an inert gas and soapy water above working pressures and be completely leak-tight. Leaks in a system containing silane will be indicated by flames. Do not attempt to extinguish but shut off source of silane immediately.
- Do not condense silane (-110° C or less). Serious accidents have occurred with liquid and solid silane.
- Evacuate piping and systems and purge at least three pipe volumes with inert gas (nitrogen, helium, and so forth) before introducing silane.
- Vent with carrier gas to outdoors (no hoods) through pipe small enough to ensure no back diffusion. Stainless steel or iron pipe is preferred.
- Use diaphragm pack-less valves with resilient seats such as Teflon.
- Remove back plates on rotameters and pressure gauge covers.
- Pressure regulators used with silane should have metal diaphragms to allow complete evacuation. All vent ports should be plumbed away from operators to a safe location.
- Do not use halogenated lubricants on silane systems. For example, Krytox 143AC and 240AC are fluorinated lubricants, which are potentially explosive with silane.
- Do not use halogenated solvents to degrease silane systems. For example, trichlorotrifluoroethane (Freon 113) is halogenated, thus potentially explosive with silane. It is recommended that silane systems be cleaned with detergents and water. In addition, it is important that the system is dry prior to charging with silane. Water and silane will react and form hydrogen gas and silicon.
- Mixtures down to 1.0 percent silane in hydrogen and/or nitrogen have been found to be spontaneously flammable when mixed with air, although at high escape velocities mixtures as high as 10 percent may not spontaneously ignite or explode until after an ignition delay time of several seconds. Venting of hydrogen-silane mixtures of any concentration shall be done as for pure silane. Preferably, they should be burned using a pilot flame.
- Ground all lines and equipment used with silane.
- Do not store reserve stocks of silane with cylinders containing oxygen or other highly oxidizing or flammable materials. Cylinders containing silane are not equipped with safety devices, and therefore shall be stored away from sources of heat to avoid the development of dangerous pressures within the cylinder.

#### 8.6.5 First Aid Treatment

Promptly remove the victim to an uncontaminated atmosphere. Keep the victim warm (not hot) and quiet. Dial 911 for medical assistance. If breathing has stopped, give artificial respiration.

# 8.7 ACETYLENE (C<sub>2</sub>H<sub>2</sub>)

Acetylene is a colorless, flammable gas slightly lighter than air. It consists of hydrogen and carbon and is highly reactive due to the unique bonding of these elements. In its free state, and at pressures above 15 psig, acetylene is thermodynamically unstable and subject to explosive decomposition. This can occur at less than 15 psig under certain conditions such as large pipe of vessel size, elevated temperatures and the presence of rust inside the piping. If improperly handled, acetylene presents an explosive potential that makes it one of the most dangerous gases in existence. Due to this inherent instability, acetylene shall be stored in and used from specially constructed cylinders. Unlike other gas cylinders, acetylene cylinders are not empty, but filled with a porous material saturated with acetone. One volume of acetone can dissolve up to 300 volumes of acetylene. Therefore, acetylene cylinders do not contain free gas but gas in solution. This allows a supply of up to 250 psig of acetylene to be put into the cylinder without raising the free gas pressure above 15 psig. Normal acetylene usage at LaRC is in the form of standard oxy-acetylene welding and cutting torches. Sufficient safety and control measures are in place for this equipment and when used properly, it has proven to be safe. However, when acetylene usage deviates from this standard method, very real dangers arise. Deviations include increasing the free pressure above 15 psig, piping acetylene into workshops and laboratories, filling empty vessels with acetylene, locating the regulator remote from the cylinder and modifying oxy-acetylene welding equipment for other uses. Acetylene is not an ordinary gas and treating it as such can produce disastrous consequences.

### 8.7.1 Properties

Specific chemical and physical properties for acetylene are presented herein.

### 8.7.1.1 Chemical Properties

Acetylene is a manufactured gas, which requires a large amount of energy to prepare. Under certain conditions - not all of them well understood - acetylene in its free state will decompose or detonate, returning to its original elements with a corresponding release of energy. Increases in pressure, temperature, vessel and piping size will increase the probability of this happening. This reaction can take two forms. The first is decomposition into carbon, hydrogen and other by-products, increasing the pressure in a closed system by a factor of 12. The second is detonation in much the same manner as ordinary explosives. This detonation results in numerous by-products, and can propagate at 2,000 meters per second and increase pressures by a factor of 100. Unlike other flammable gases, which require an oxidizer and are chemically unreactive when confined in a vessel, acetylene contains within itself all that is required to produce decomposition or detonation. Acetylene, when burned with oxygen, produces the hottest flame of all the hydrocarbon gases. The flammability range for acetylene in

atmospheric air is 2.5 to 80 percent. The upper range can increase to 94 percent if mixed with oxygen.

### 8.7.1.2 Physical Properties

The physical properties of acetylene can be found in various works on gases and chemistry ("Matheson Gas Data Book," "Handbook of Compressed Gas," "Encyclopedia of Chemical Technology," etc.).

### 8.7.2 Toxicity

Pure acetylene is not toxic and is odorless. Some references state it has an agreeable, ether-like odor. In higher concentrations, acetylene acts as an intoxicant and an anesthesia. At one time, mixtures of acetylene and oxygen were used for this purpose. Concentrations of 10 to 40 percent will cause marked intoxication and unconsciousness. Acetylene with a distinct garlic-like odor is pure and may contain appreciable amounts of phosphine - the source of the odor. A concentration of 0.3 ppm of phosphine in air is considered hazardous. Acetylene can also produce asphyxiation by replacing the oxygen in the air. However, before either intoxication or asphyxiation could occur, the affected area would be filled with a highly explosive mixture, which presents a much greater danger. No threshold limit value (TLV) for acetylene has been recommended because this would depend on the available oxygen.

### 8.7.3 Safety Measures

Safety measures shall include:

- In addition to special safety considerations, acetylene shall be treated as any other flammable gas under pressure.
- Acetylene cylinders shall be used in an upright position, with a regulator limited to 15-psig maximum output. The regulator shall always be attached directly to the bottle.
- Oxy-acetylene welding and cutting equipment shall be assembled and used according to current safety regulations. It shall not be modified in any way for maintenance or shop work.
- Oxy-acetylene welding and cutting equipment shall not be modified for, or used in, research experiments.
- If acetylene is to be used in any manner other than from the standard oxyacetylene welding and cutting units or for any purpose other than welding and
  cutting, regardless of pressure, the design work shall be done by Facility
  Engineering. This includes connecting or manifolding bottles together. The
  design shall be reviewed and approved by the SFAB, SMAO and the PHMC
  before work begins. The Systems Operation Committee shall inspect and
  approve the finished system before use.
- Work Control shall route to SFAB, SMAO all requests for acetylene installations.

# 8.7.4 Medical Treatment

Dial 911 for medical assistance. First degree and minor second-degree thermal burns from fires should be immersed in cool water for 30 minutes. Major second degree and third degree burns should be covered in the cleanest material available. Seek immediate aid of a physician. Persons suffering from lack of oxygen should be moved to areas with normal atmosphere. Assisted respiration and supplemental oxygen should be given if the victim is not breathing.

# **LPR 1710.12 APPENDICES**

### A. OSHA REGULATED SUSPECT AND POTENTIAL CARCINOGENS

The chemical listed herein are considered to be particularly hazardous substances as defined in 29 CFR 1910.1450, and they are considered regulated chemicals for the purpose of this handbook.

### A.1 CHEMICAL-SPECIFIC OSHA REGULATIONS

The following chemical-specific OSHA regulations are found in 29 CFR 1910.

OSHA Regulation	Material	CAS Number
1910.1001	Asbestos	77500 00 0
	Tremolite	77536-68-6
	Anthophyllite	77536-67-5
	Actinolite	77536-66-4
	Amosite	12172-73-5
	Chrysolite	12001-29-5
4040 4000	Crocidolite	12001-28-4
1910.1002	Coal Tar Pitch Volatiles (except Asphalt)	65996-93-2
1910.1003	4-Nitrobiphenyl	92-93-3
1910.1004	Alpha-Naphthylamine_	134-32-7
1910.1006	Methyl Chloromethyl Ether	107-30-2
1910.1007	3,3'-Dichlorobenzidine (and salts)	91-94-1
1910.1008	bis-Chloromethyl Ether	542-88-1
1910.1009	beta-Naphthylamine	91-59-8
1910.1010	Benzidine	92-87-5
1910.1011	4-Aminobiphenyl	92-67-1
1910.1012	Ethyleneimine	151-56-4
1910.1013	beta-Propiolactone	57-57-8
1910.1014	2-Acetylaminofluorene	53-96-3
1910.1015	4-Dimethylaminoazobenzene	60-11-7
1910.1016	N-Nitrosodimethylamine	62-75-9
1910.1017	Vinyl Chloride	75-01-4
1910.1018	Inorganic Arsenic	7440-38-2
1910.1025	Lead	7439-92-1
1910.1027	Cadmium (MDA)	7440-43-9
1910.1028	Benzene	71-43-2
1910.1029	Coke oven emission	None
1910.1043	Cotton dust	None
1910.1044	1,2-dibromo-3-chloropropane (DBCP)	96-12-8
1910.1045	Acrylonitrile	107-13-1
1910.1047	Ethylene Oxide	75-21-8
1910.1048	Formaldehyde	50-00-0
1910.1050	Methylenedianiline (MDA)	101-77-9
1910.1051	1.3-Butadiene	106-99-0
1910.1052	Methylene Chloride	75-09-2

#### B. DEFINITIONS AND TERMINOLOGY

**Acute Exposure** Short duration contact, typically minutes or hours.

**Asphxiatory** Capable of causing injury by depriving the body of

oxygen. Substances producing this effect by dilution of

atmospheric oxygen are referred to as simple

asphyxiants.

**Temperature** 

**Narcotic** 

Autoignition The temperature at which a material will selfignite and

sustain combustion in absence of a spark or flame.

Carcinogenic Capable of causing cancer. (NOTE: MSDSs are required

to list any carcinogens present.)

**Chronic Exposure** Long duration contact, typically days, months, or years.

**Cryogenic** Maintained at extremely low temperatures.

**Explosive Range** Range of concentration of a gas or vapor in air above

and below which the mixture will not burn. Usually described as Lower and Upper Explosive Limits (LEL

and UEL) and expressed in percentage.

Flash Point Lowest temperature at which a liquid will give off enough

flammable vapor at or near its surface so that it will ignite

upon introduction at an ignition source.

**IDLH** Immediately Dangerous to Life or Health Concentration.

Concentration at which serious health impairments, or irreversible biological effects possibly leading to death in a period of seconds or several days later, could occur.

Capable of causing depression of the central nervous

system; drowsiness, stupor, loss of coordination,

unconsciousness.

PEL (Permissible Airborne concentration exposure standards are specified by Federal Law (OSHA, 29 CFR). Concentrations may

by Federal Law (OSHA, 29 CFR). Concentrations may be for 8-hour workdays, or shorter periods (usually 15

minutes). (See also Threshold Limit Values.)

# TLV (Threshold Limit Value)

Airborne concentration at or below which it is believed nearly all workers may be repeatedly exposed day after day with no adverse effect. Usually expressed in parts per million (ppm) for gases or vapors and milligrams per cubic meter (mg/m3) for dusts, fumes, and mists. Threshold Limit Values are specified by the American Conference of Governmental Industrial Hygienists and several have been adopted for use by OSHA.

### **Vapor Density**

Ratio of the specific gravity of a vapor to that of air. Materials having a vapor density greater than one are heavier than air.

# **Vapor Pressure**

The measure of tendency for a liquid to go into a gaseous state. Usually expressed in millimeters of mercury (mm Hg). More volatile materials have higher vapor pressures.